

FUEL REFORMER CATALYST AND ABSORBENT MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is related to U.S. Provisional Patent Application Serial No. _____ by Hampden-Smith et al., entitled CARBON DIOXIDE ABSORBENT MATERIALS AND METHODS FOR MAKING SAME, and filed on November 26, 2003, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

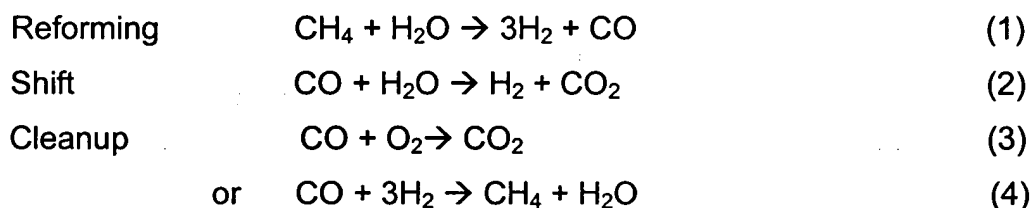
1. Field of the Invention

15 The present invention relates to particulate materials that are useful for fuel reformers, such as catalyst materials for hydrogen production from carbon-based fuels and absorbent materials for the removal of acid gases such as CO₂ and H₂S from gas streams. The particulate materials can be produced by spray processing of precursors to form a powder batch. The present invention is also directed to fuel reformers incorporating the particulate materials and methods for using the materials. The present invention is also directed to the combination of a highly reversible, high-capacity
20 CO₂ absorbent with steam reforming and/or water gas shift catalysts to achieve single step conversion of hydrocarbon fuels to hydrogen with a high conversion efficiency.

2. Description of the Related Art

25 Hydrogen (H₂) is an important material in the chemical, petroleum and energy industries. In the chemical and petroleum industries, hydrogen is used for the manufacture of ammonia (NH₃) and methanol (CH₃OH), and is used in a variety of petroleum hydrotreating processes. A growing demand for hydrogen is forecast in the future, particularly for petroleum refining of heavy, high-sulfur crude oil. Hydrogen is also an environmentally clean energy source for the generation of electric power and
30 space heating, and a substantial increase in hydrogen demand is expected in the near future.

Steam reforming, including steam-methane reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR) are the major processes for hydrogen production from fossil-based fuels such as natural gas, and are expected to remain processes of choice for the next several decades. These fuel-processing technologies involve multiple steps and severe operating conditions. For example, SMR involves the endothermic reaction of methane (e.g., natural gas) with water to form H₂ and carbon monoxide (CO). The primary reformer operates at a temperature of approximately 800°C to 850°C and about 20 atm of pressure, and large quantities of supplemental fuel must be burned to supply the energy necessary to maintain the reformer temperature. Further, the reforming step is followed by at least one water gas shift (WGS) reactor to increase the H₂ content and reduce the CO content. This is followed by CO cleanup using selective oxidation, hydrogen membrane separation, pressure swing absorption or methanation. The reactions that occur during SMR of methane (CH₄), the major component of natural gas, are illustrated by Equations 1 to 4:



Another commercially available method for the production of hydrogen from hydrocarbons is partial oxidation (POX). According to this method, CH₄ or a similar hydrocarbon feed stock is oxidized to produce CO and H₂ in accordance with the reaction illustrated by Equation 5:



This reaction is exothermic and therefore no heat is required. A typical POX system includes a POX reactor, followed by a shift reactor and a H₂ purification step. A POX reactor is more compact than a steam reformer since no additional heat must be added. The efficiency of the POX reactor is relatively high, however, POX systems are typically

less energy efficient than SMR because of the utilization of higher temperatures and the problem of heat recovery.

Auto thermal reforming (ATR) combines some of the features of SMR and POX. In ATR, a hydrocarbon feed such as CH_4 is reacted with both steam and air to produce an H_2 -rich gas. Both the SMR and POX reactions take place (Equations 1 and 5). With the correct mixture of input fuel, air and steam, the POX reaction supplies all the heat needed to drive the catalytic SMR reaction. However, as with SMR and POX systems, a WGS reactor and a H_2 purification stage are required to remove carbon oxides.

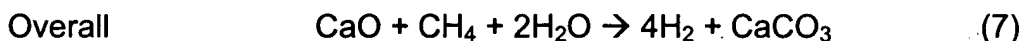
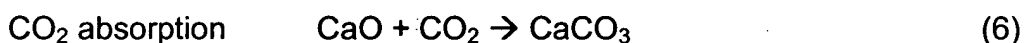
Fuel cells provide electricity through chemical oxidation-reduction reactions and have tremendous advantages over other types of power generation devices in terms of energy efficiency and environmental compatibility. For low temperature applications, the most promising type of fuel cell is the proton exchange membrane (PEM) fuel cell, which employs H_2 as a fuel in the anode and O_2 as an oxidant in the cathode. However, the cost of constructing the distribution infrastructure to safely transport pure H_2 gas over large distances presents an economic barrier to the exploitation of fuel cells, particularly for the transportation sector. Therefore, distributed production by smaller reforming systems that convert hydrocarbons to H_2 gas is a more viable option for the near future. However, conventional fuel-processing technologies for H_2 production from hydrocarbons are unsatisfactory for providing H_2 to PEM fuel cells due to low reforming efficiencies resulting from the multiple steps that are required and the severe operating conditions that are required, as is discussed above. Further, the reformat typically has a low H_2 content (45 to 50 mol.% on a dry basis) and a high CO and CO_2 content. The reformat can also include other gases, such as N_2 , depending on the reforming method.

The low H_2 content in the reformat reduces the fuel cell performance and requires that greater amounts of expensive Pt and PtRu catalysts and membrane materials be utilized for reasonable system efficiency as compared to fuel cells operating on pure H_2 . The high levels of CO_2 in the reformat also cause two additional problems. The CO_2 converts to CO in the PEM stack due to the reverse water gas shift reaction (reverse of Equation 2) and the CO can poison the catalyst. Also, the acidic

nature of CO₂ and water solutions promotes a number of reactions that can reduce the useful lifetime of the PEM stacks by greater than 50%.

The deficiencies of conventional fuel reforming processes can be overcome to a certain extent by following the WGS step with amine scrubbing, hydrogen membrane separation and/or pressure swing adsorption (PSA). With amine scrubbing it is often necessary to further reduce the concentration of carbon oxides to trace levels by methanation. PSA requires operation at a significant pressure, which lowers system efficiency and produces a tail gas containing 25% to 30% of the H₂ produced during column blowdown and purge. While the energy content of the tail gas can be recovered and used in the reforming process it is often the case that the energy content of the combined fuel cell anode tail gas and the purification tail gas is greater than the energy required by the reforming process.

A variety of approaches have been explored to develop a fuel processing technology that uses simple chemical processes, has low energy consumption and generates high purity H₂. These include the application of reaction-separation membranes and the application of absorption materials. One promising approach is absorption enhanced reforming (AER). AER combines a SMR catalyst and a CO₂ absorbent (e.g., CaO) in a single reactor so that reforming, shift, and CO₂ absorption occur simultaneously.



Many potential benefits over conventional reforming have been demonstrated using AER. These include: (i) reforming at a significantly lower temperature (about 600°C), while achieving an increased conversion of CH₄ to H₂; (ii) lower capital cost as compared to conventional SMR; (iii) producing H₂ at feed gas pressure (200 to 400 psig) and at relatively high purity (>95%) directly from the reactor; (iv) reducing or even eliminating downstream purification steps; (v) minimizing side reactions and increasing catalyst lifetime; (vi) reducing the excess steam used in conventional reforming, particularly when treating heavy fuels; and (vii) effective fixing of CO₂.

It should be noted that various terminology has been used in the literature to describe the reaction of CO₂ and a solid material such as CaO. Among the terms used are adsorption, absorption, sorption and fixing of CO₂. In general, none of these terms precisely describes this complex process, which starts with adsorption of the CO₂ onto the surface of a solid, followed by a chemical conversion of the solid and expansion of this process into the bulk of the solid. Therefore, the terms adsorption, absorption and fixing (to describe the process), and adsorbent and absorbent (to describe the solid material) are used interchangeably within the present specification.

The use of AER for H₂ production for use in a fuel cell has been disclosed in U.S. Patent Application Publication No. 20020155329 by Stevens. More recently, the benefits of this approach for hydrogen production from solid fuels such as biomass and coal have also been demonstrated by S. Lin et al. (Fuel 2002, 81, 2079).

There are a variety of CO₂ absorption materials available for AER. Reaction-based CO₂ absorption materials such as CaO-based absorbents are preferred because these types of materials typically have much higher equilibrium capacities than other absorbents. For example, under ideal conditions methylethanolamine captures 6g/100g (grams of CO₂ per 100 gram of material), silica gel absorbs 1.32g /100g, and activated carbon absorbs 8.8g/100g. Materials used for PSA such as K₂CO₃/Hydrotalcite can only remove a small portion of CO₂, about 1.98g/100g. In contrast, CaO can capture 78.57g/100g. Even assuming only a 50 wt.% capacity over repeated cycles, the value of 39.3 g/100g for AER is 5 to 10 times higher than the above absorbents.

The conversion of hydrocarbons in the presence of steam and a CO₂ absorbent can be traced back to as early as 1868. Recently some results for hydrogen production using this concept have been reported by: D. P. Harrison et al, Chemical Engineering Science 1999, 54, 3543; V. K. Ravi et al., Proceeding of the 2002 U.S. DOE Hydrogen Program Review NREL/CP610-32405; M. Spectht et al., Hydrogen Energy Progress XIII, Z.Q. Mao, T. N. Veriroglu (Eds.), 2000, 1203; and J. R. Hufton et al., Proceedings of the 1995 U.S DOE Hydrogen Program Review, 1995, 1, 815. The CO₂ absorbents typically used for AER have poor reactivity, low CO₂ capacity, and poor recyclability.

The key to successfully commercialize AER methods is to develop an absorbent with

high activity and capacity, and particularly with high recyclability to maintain sufficient activity and capacity over numerous carbonation and decarbonation cycles.

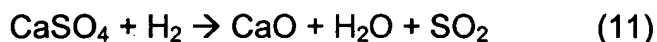
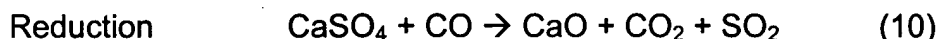
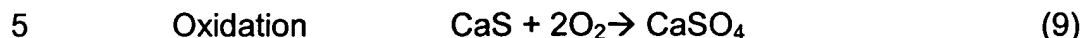
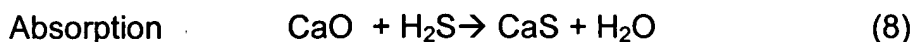
The absorbent materials have other applications in addition to AER. The increasing use of fossil fuels to meet energy needs has led to higher CO₂ emissions into the atmosphere and CO₂ emissions from direct combustion of fossil fuels account for one-half of the greenhouse effect that causes global warming. It is therefore necessary to develop cost-effective CO₂ management schemes to curb CO₂ emissions. Many CO₂ management schemes consist of three parts: separation, transportation, and sequestration. The capture of CO₂ accounts for about 75% of the total cost of CO₂ management, and imposes a severe energy requirement on fossil fuel-based power plants, reducing their net electricity output by as much as 37%. The costs associated with current CO₂ separation technologies necessitate the development of economical alternative.

Integrated gasification combined cycle (IGCC) power generation systems hold great promise for producing electric power efficiently and economically. Instead of direct combustion, coal is gasified by means of enriched air, O₂, and/or H₂O to obtain a concentrated coal gas. After cleanup, the coal gas is used to fire a gas turbine. The hot exhaust from the gas turbine is passed to a boiler to generate steam, which is then used to drive a steam turbine.

Coal includes sulfur as an impurity, which upon gasification typically enters the coal gas stream as hydrogen sulfide (H₂S). It has been common practice to cool the gas below 77°C to remove H₂S by wet scrubbing. However, this practice reduces the overall efficiency of the power generation plant significantly. Hot gas cleanup methods capable of operating at temperatures close to the gasifier outlet temperature, which may range from 725°C to 1325°C, would increase the overall energy conversion efficiency. While various absorbents have been proposed for desulfurizing hot coal gas, few are effective at such high temperatures.

It is known that zinc-based materials such as zinc oxide (ZnO) are highly effective for removing H₂S, but their use is limited to temperatures below 650°C. At higher temperatures, calcium-based absorbents are promising because the reaction of

CaO with H₂S is both thermodynamically and kinetically favorable. The reactions are illustrated by Equations 8 to 11.



It has been proven experimentally and thermodynamically by van der Ham et al.
10 (Ind. Eng. Chem. Res., 1996, 35, 1487) that the H₂S content of gas produced by an air-
and steam-blown coal gasifier operating under typical conditions can be reduced to 20
ppmv by employing CaO in highly reducing conditions at a temperature higher than
800°C. Regeneration can be accomplished at a temperature above the absorption
temperature by employing a cyclic oxidation and reduction process, as is disclosed by
15 S. B. Jagtap et al., Energy Fuels, 1996, 10, 821 and in U.S. Patent No. 6,083,862 by
Wheelock.

Natural CaO-based absorbents such as limestone and dolomite are plentiful and
inexpensive, but they are soft and friable and do not stand up well to handling and
recycle use. To improve the recyclability, some work has been focused on the
20 pelletizing of limestone by using different binders. See, for example, U.S. Patent No.
4,316,813 by Voss et al. Some work also focused on the modification of natural
materials such as dolomite to tailor the physicochemical properties of the material. The
synthesis of a CaO-based absorbent through boiling of CaO into Ca(OH)₂ or the
carbonation of calcium salt solution such as calcium nitrate or Ca(OH)₂ into calcium
25 carbonate, then decomposition of the carbonate into CaO has been disclosed by L.S.
Fan et al., Ind. Eng. Chem. Res., 1999, 38, 2283. Others have disclosed the
preparation of CaO-based materials by aerogel methods.

The foregoing methods generally result in limited control over the composition
and microstructure of the powders. The morphology and surface properties such as
30 surface area, pore volume and pore size are among the characteristics that have a
critical impact on the performance of the absorbent. This is due to the nature of the

reactions that occur. First, carbonation takes place on the external and internal surfaces of CaO-based absorbent, which forms a carbonate layer. Then, the chemical reaction advances with the diffusion of CO₂ through the carbonate layer into the unreacted core CaO active sites. Therefore, higher reactivity and faster kinetics can be expected for small particle size CaO due to the higher surface to bulk ratio of the absorbent species. A more porous structure will also lead to higher reactivity and recyclability, and a lower decarbonation temperature due to the easier CO₂ diffusion into or out of the outer carbonate layer.

It would be advantageous to provide a method for producing absorbent powders that would enable control over the powder characteristics such as particle size, surface area and pore structure as well as the versatility to accommodate compositions which are either difficult or impossible to produce using existing production methods. It would be particularly advantageous if such powders could be produced in large quantities on a substantially continuous basis. Further value can be derived from these powders if they can be incorporated into structures that can be integrated into reactor beds that enable a suitable combination of high space velocity and high absorption capacity while retaining their performance characteristics. Such structures include coatings, such as wash coatings on highly porous monoliths, pellets that have pore structures that retain the performance of the powders and also coatings or impregnation of the powder particles into other structures such as metals, metal oxides, textiles or cloths, which may provide beneficial heat transfer characteristics.

SUMMARY OF THE INVENTION

According to one embodiment of the present invention, a method for the conversion of a carbon-based fuel to a hydrogen-rich product gas is provided. The method includes the steps of providing a carbon-based fuel, converting the carbon-based fuel to an intermediate gas product by contacting the fuel with at least a first conversion catalyst, contacting the intermediate gas product with an absorbent material to absorb CO₂ and form a hydrogen-rich gas, extracting the hydrogen-rich gas from the contacting step and regenerating the absorbent. The foregoing steps are repeated at

least ten times wherein the absorbent material retains at least about 50 mol. % of its theoretical absorption capacity after each of the repeating steps.

According to another embodiment, a method for the conversion of a carbon-based fuel to a hydrogen-rich product gas is provided. The method includes providing a carbon-based fuel, converting the carbon-based fuel to an intermediate gas product by contacting the fuel with at least a first conversion catalyst, contacting the intermediate gas product with an absorbent material to absorb CO₂ and form a hydrogen-rich gas, extracting the hydrogen-rich gas from the contacting step and regenerating the absorbent. The foregoing steps can be repeated at least ten times wherein the total mass of the absorbent material retains at least about 10 grams CO₂ per 100 grams of unreacted absorbent after each cycle.

According to yet another embodiment, a method for the conversion of a carbon-based fuel to a hydrogen-rich product gas is provided. The method includes the steps of providing a carbon-based fuel and steam, converting the fuel and steam to an intermediate gas product by contacting the fuel and steam with at least a first conversion catalyst, contacting the intermediate gas product with an absorbent material to absorb CO₂ and form a hydrogen-rich gas, extracting the hydrogen-rich gas from the contacting step and regenerating the absorbent. At least the absorbent material is a pelletized form and the foregoing steps can be repeated at least 50 times wherein the absorbent material retains at least about 20 mol. % of its theoretical CO₂ absorption capacity after each cycles.

According to another embodiment, a method for absorption enhanced reforming of a carbon-based fuel is provided. The method includes providing a carbon-based fuel, contacting the fuel with at least a first conversion catalyst to catalyze the formation of hydrogen and with a pelletized absorbent compound having a first bulk density, wherein the pelletized absorbent is converted to a carbonized absorbent having a second bulk density and regenerating the carbonized absorbent to form a regenerated absorbent having a third bulk density, wherein the third bulk density is greater than the first bulk density.

According to another embodiment of the present invention, an absorbent material for the absorption of CO₂ is provided which includes an absorbent compound and a metal oxide, wherein the absorbent material has a surface area of at least about 5 m²/g.

5 According to another embodiment of the present invention, a CO₂ absorbent material is provided including particulates of a calcium-containing compound selectively doped with at least about 0.1 at.% of an additional element selected from the monovalent and divalent and polyvalent metals, the particulates having a surface area of at least 5 m²/g.

10 According to another embodiment of the present invention, a steam-reforming catalyst is provided. The steam-reforming catalyst includes a particulate support structure and a metal dispersed on the support structure wherein the reforming catalyst achieves at least about 90% of the theoretical thermodynamic conversion of methane to hydrogen at a temperature of 600°C, a H₂O:C ratio of 3:1 and a gas hour space velocity (GHSV) of 5000 hour⁻¹ in the absence of an absorbent for CO₂.

15 According to another embodiment of the present invention, a particulate composite material is provided which includes an absorbent phase adopted to absorb CO₂ and a catalyst phase selected from the group consisting of a reforming catalyst phase and a water-gas shift catalyst phase.

20 According to another embodiment of the present invention, a method for the fabrication of a particulate calcium oxide-containing absorbent material is provided. The method includes the steps of providing a precursor solution including at least a first precursor to a calcium oxide-containing compound, atomizing the precursor solution to form precursor droplets and heating the precursor droplets to form a particulate calcium oxide-containing compound.

25 According to another embodiment of the present invention, a method for the fabrication of a calcium oxide-containing absorbent material is provided. The method includes the steps of providing a precursor solution including at least a first precursor to an intermediate calcium compound, atomizing the precursor solution to form precursor droplets, heating the precursor droplets to form a particulate intermediate calcium compound, the calcium compound having a theoretical density that is less than the
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theoretical density of calcium oxide, and converting the intermediate calcium compound to a calcium oxide-containing absorbent material.

According to another embodiment of the present invention, a method for the fabrication of an absorbent material including an absorbent phase and a metal oxide is provided. The method includes providing a precursor solution including at least a first precursor to an absorbent compound and a solvent. A particulate metal oxide is mixed with the precursor solution and the solvent is removed from the precursor mixture. The precursor mixture is heated to at least partially react the active absorbent compound precursor and form the absorbent material.

According to another embodiment of the present invention, a method for the fabrication of supported reforming catalyst particles is provided. The method includes forming a precursor solution including a metal precursor and an alumina precursor, atomizing the precursor solution to form precursor droplets and heating the precursor droplets to convert at least the metal precursor to metal-containing clusters dispersed on the alumina.

According to another embodiment of the present invention, a method for the fabrication of composite particles including an absorbent phase and a catalyst phase is provided. The method includes the steps of forming a precursor solution including a liquid, a precursor to an absorbent phase and a precursor to a catalyst phase. The precursor solution is atomized to form precursor droplets and the precursor droplets are heated to remove liquid from the droplets and form composite particles.

According to another embodiment of the present invention, a method for the fabrication of composite particles including an absorbent phase and a catalyst phase is provided. The method includes forming a particulate suspension, where the particulate suspension includes a liquid, a first particulate phase comprising an absorbent phase or an intermediate precursor to an absorbent phase and a second particulate phase comprising a catalyst phase. The particulate suspension is atomized to form suspension droplets and the droplets are heated to remove liquid from the droplets and form composite particles.

According to another embodiment of the present invention, a pellet is provided that includes at least about 5 wt. % of a particulate intermediate compound to an

absorbent compound, wherein the particulate intermediate compound has a theoretical density that is not greater than the theoretical density of the absorbent compound and wherein the particulates are substantially spherical.

5 According to another embodiment of the present invention, a pellet for the absorption of CO₂ is provided. The pellet includes composite particulates of a calcium compound and from about 1 wt. % to about 40 wt. % of a metal oxide selected from the group consisting of aluminum oxides and titanium oxides, wherein the particulates are substantially spherical.

10 According to another embodiment of the present invention, a pellet adapted for the absorption enhanced reforming of a carbon-based fuel is provided. The pellet includes a particulate absorbent material and a particulate catalyst material.

15 According to yet another embodiment of the present invention, a pellet adapted for the absorption enhanced reforming of a carbon-based fuel is provided. The pellet includes composite particulates including an absorbent phase adapted to absorb CO₂ and a catalyst phase selected from the group consisting of a reforming catalyst and a water-gas shift catalyst.

These and other embodiments of the present invention are described in more detail herein below.

20 DESCRIPTION OF THE DRAWINGS

Fig. 1 schematically illustrates a spray pyrolysis method for the fabrication of particles according to an embodiment of the present invention.

Fig. 2 schematically illustrates a spray conversion method for the fabrication of particles according to an embodiment of the present invention.

25 Fig. 3 schematically illustrates a post-processing method for the fabrication of particles according to an embodiment of the present invention.

Fig. 4 illustrates the calculated equilibrium gas composition for steam reforming of methane in the presence of a CO₂ absorbent such as CaO.

30 Fig. 5 illustrates the calculated equilibrium gas composition for steam reforming of methane without a CO₂ absorbent.

Fig. 6 illustrates a process of the absorption of a contaminant from a gas stream with a regenerating step.

Fig. 7 illustrates the aggregate particle morphology of a particulate absorbent material according to an embodiment of the present invention.

5 Fig. 8 illustrates the aggregate particle morphology of a particulate absorbent material according to an embodiment of the present invention.

Fig. 9 illustrates the aggregate particle morphology of a supported absorbent material according to an embodiment of the present invention.

10 Fig. 10 illustrates the aggregate particle morphology of an absorbent material according to an embodiment of the present invention.

Fig. 11 illustrates the structure of a supported composite particle including a water gas shift catalyst and reforming catalyst according to an embodiment of the present invention.

15 Fig. 12 illustrates the structure of a composite absorbent/catalyst particle according to an embodiment of the present invention.

Fig. 13 illustrates the particle size distribution of absorbent powders according to the present invention compared to the prior art.

Fig. 14 illustrates the BET surface area of absorbent powders according to the present invention compared to the prior art.

20 Fig. 15 illustrates the pore volume of absorbent powders according to the present invention compared to the prior art.

Fig. 16 illustrates the carbonation and decarbonation kinetics of a commercial CaO powder according to the prior art.

25 Fig. 17 illustrates the absorption capacity of a commercial CaO absorbent powder over 26 cycles.

Fig. 18 illustrates the particle size distribution of a commercial CaO absorbent powder before and after 27 cycles.

Fig. 19 illustrates the pore volume, BET surface area and average pore size of a commercial CaO absorbent powder before and after 27 cycles.

Fig. 20 illustrates the absorption capacity in terms of CaO reaction fraction of CaO-based absorbents over multiple cycles according to the present invention compared to the prior art.

5 Fig. 21 illustrates the carbonation and decarbonation kinetics of CaO-based absorbents according to the present invention compared to the prior art.

Fig. 22 illustrates the particle size distribution of absorbent powders according to the present invention.

Fig. 23 illustrates the pore volume, BET surface area and average pore diameter for absorbent powders according to the present invention.

10 Fig. 24 illustrates the absorption capacity in terms of CaO reaction fraction of absorbent powders according to the present invention over multiple cycles.

Figs. 25(a) and 25(b) illustrate SEM photomicrographs of a commercial CaO powder before and after 27 cycles.

15 Figs. 26(a) and 26(b) illustrate SEM photomicrographs of an absorbent powder according to the present invention before and after 12 cycles.

Figs. 27(a) and 27(b) illustrate SEM photomicrographs of an absorbent powder according to the present invention before and after 12 cycles.

Fig. 28 illustrates the particle size distribution of absorbent powders according to the present invention before and after 12 cycles.

20 Fig. 29 illustrates the absorption capacity in terms of CaO reaction fraction of absorbent powders according to the present invention over 12 cycles.

Fig. 30 illustrates the carbonation and decarbonation kinetics of several absorbent powders according to the present invention.

25 Fig. 31 illustrates the carbonation and decarbonation kinetics of a composite absorbent powder according to the present invention.

Fig. 32 illustrates the adsorption capacity over 12 cycles for 2 absorbent materials according to the present invention.

Fig. 33 illustrates the carbonation and decarbonation kinetics of several absorbent powders according to the present invention.

30 Fig. 34 illustrates the particle size distribution of absorbent powders according to the present invention before and after 12 cycles.

Fig. 35 illustrates the pore volume, BET surface area and average pore diameter of absorbent powders according to the present invention before and after 12 regeneration cycles.

5 Fig. 36 illustrates the methane conversion over steam reforming catalysts according to the present invention compared to a prior art catalyst.

Fig. 37 illustrates the methane conversion over steam reforming catalysts according to the present invention compared to a prior art catalyst.

Fig. 38 illustrates the methane conversion over steam reforming catalysts according to the present invention compared to a prior art catalyst.

10 Fig. 39 illustrates the methane conversion over steam reforming catalysts according to the present invention compared to a prior art catalyst.

Fig. 40 illustrates the absorption capacity in terms of CaO reaction fraction of multi-functional composite powders according to the present invention.

15 Fig. 41 illustrates the carbonation and decarbonation kinetics of multi-functional composite powders according to the present invention.

Fig. 42 illustrates the absorption capacity over 92 cycles in terms of CaO reaction fraction of a multi-functional composite powder according to the present invention.

Fig. 43 illustrates the absorption capacity over 92 cycles of a multi-functional composite powder according to the present invention.

20 Fig. 44 illustrates the carbonation and decarbonation kinetics for a multi-functional composite powder according to the present invention.

Fig. 45 illustrates the absorption capacity in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention.

25 Fig. 46 illustrates the absorption capacity of pelletized absorbent powders according to the present invention.

Fig. 47 illustrates the carbonation and decarbonation kinetics of pelletized absorbent powders according to the present invention.

Fig. 48 illustrates the absorption capacity in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention over 116 cycles.

30 Fig. 49 illustrates the absorption capacity of pelletized absorbent powders according to the present invention over 116 cycles.

Fig. 50 illustrates the absorption capacity in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention over multiple cycles.

Fig. 51 illustrates the absorption capacity of pelletized absorbent powders according to the present invention over multiple cycles.

5 Fig. 52 illustrates the absorption capacity in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention over multiple cycles.

Fig. 53 illustrates the absorption capacity of pelletized absorbent powders according to the present invention over multiple cycles.

10 Fig. 54 illustrates the absorption capacity in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention over multiple cycles.

Fig. 55 illustrates the absorption capacity over 66 cycles of pelletized absorbent powders according to the present invention.

Fig. 56 illustrates the absorption capacity over 66 cycles in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention.

15 Fig. 57 illustrates the absorption capacity over 66 cycles of pelletized absorbent powders according to the present invention.

Fig. 58 illustrates the absorption capacity over 66 cycles in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention over multiple cycles.

20 Fig. 59 illustrates the absorption capacity over 66 cycles of pelletized absorbent powders according to the present invention.

Fig. 60 illustrates the absorption capacity over 64 cycles in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention.

25 Fig. 61 illustrates the absorption capacity over 64 cycles of pelletized absorbent powders according to the present invention.

Fig. 62 illustrates the absorption capacity over 64 cycles in terms of CaO reaction fraction of pelletized absorbent powders according to the present invention.

Fig. 63 illustrates the conversion efficiency of a composite absorbent/catalyst material according to an embodiment of the present invention.

30 Fig. 64 illustrates the conversion efficiency of a composite absorbent/catalyst material according to an embodiment of the present invention.

DESCRIPTION OF THE INVENTION

The present invention is directed to improved materials and methods for making materials that are particularly useful in absorption-enhanced reforming (AER) processes for the production of a hydrogen-rich gas from carbon-based fuels such as hydrocarbons. The materials can include, but are not limited to, CaO-based materials for CO₂ absorption and supported Rh/Al₂O₃ for steam reforming and water-gas shift catalysts.

10 Overview of Spray Processing

The materials of the present invention are preferably fabricated by spray drying, spray conversion or spray pyrolysis methods, which are collectively referred to herein as spray processing. The spray processing methods of the present invention are capable of producing a wide variety of materials and microstructures. The major attribute of this approach is the ability to fabricate compositions and microstructures that cannot be fabricated by other powder manufacturing methods, combined with the ability to economically produce high volumes of material. The flexibility to fabricate unique combinations of compositions and microstructures comes from the fact that spray processing combines aspects of both liquid phase and solid state processing.

20 Spray processing generally includes the steps of providing a precursor composition, typically in a flowable liquid form. The precursor composition typically includes at least a precursor to the absorbent or catalytic material, which are collectively referred to herein as an active material. In the case of supported active materials, the precursor composition can also include a precursor to or a suspension of the support phase. The precursor composition is atomized to form a suspension of liquid precursor droplets and the liquid is removed from the liquid precursor droplets, such as by heating, to form the powder. Typically, at least one component of the liquid precursor is chemically converted into a desired component of the powder.

30 CaO is a preferred absorbent material according to one embodiment of the present invention. Spray processing precursors for CaO can be selected from calcium metal salts such as calcium nitrate Ca(NO₃)₂, calcium oxalate, calcium acetate and

calcium hydroxide, with calcium nitrate being particularly preferred for some applications. It is often desirable to form the CaO with a high level of porosity or crystallinity and therefore it may be advantageous to include a morphology enhancing agent in the precursor composition to enhance the porosity or crystallinity of the powder.

- 5 Morphology enhancing agents can be selected from lactic acid, glycine, alcohols, ammonium nitrate, polymers and carbonyldiurea. The amount of porosity or crystallinity enhancing agent in the precursor composition can be varied from about 5 vol.% to about 40 vol.%.

Other materials can be included in the absorbent materials according to the present invention, as is discussed in more detail below. Included among these are aluminum oxides, magnesium oxides, silicon oxides, titanium oxides and mixtures of two or more oxides. Precursors for such materials can include nitrate salts such as aluminum nitrate or magnesium nitrate as well as others. In addition, the material can include other metals such as iron, magnesium, zinc and copper. Precursors for these metals can be selected from the metal nitrates, sulfates, carbonates, acetates, oxalates, hydroxides and metal oxide nanoparticles, including fumed metal oxides.

Preferred steam reforming catalysts include rhodium (Rh) metal dispersed on a support such as alumina (Al_2O_3). Accordingly, the Rh precursor can preferably be selected from rhodium acetate $\text{Rh}(\text{OAc})_3$ and rhodium nitrate $\text{Rh}(\text{NO}_3)_3$. The active metal species can also include metals such as nickel (Ni), platinum (Pt) and palladium (Pd) and precursors for these metals can be selected from nitrates, amines, hydroxides, chlorides and the like.

The spray processing methods can combine the drying of the precursors and the conversion to the active material in one step, where both the removal of the solvent and the conversion of a precursor occur essentially simultaneously. This method is referred to as spray pyrolysis, and is schematically illustrated in Fig. 1. In another embodiment, the spray processing method achieves the drying of the precursors and a partial conversion of the precursors to an intermediate compound. This method is schematically illustrated in Fig. 2. The complete conversion to the active material and/or the crystallization of the material can occur in a second step, such as the step that is schematically illustrated in Fig. 3. This second step is referred to herein as post-

processing. Thus, spray drying or spray conversion is followed by conventional heating or calcination, e.g., a method illustrated in Fig. 2 followed by a method such as that illustrated in Fig. 3. By varying reaction time, temperature and type of precursors, the spray processing methods can produce powder morphologies and active material structures that yield improved performance.

When the active material phase is dispersed on an inert support in the form of active material clusters, the precursor composition can include particulates that form the inert support phase. According to the present invention, such particulates can include particulate carbon or particulate aluminum oxide, such as particulate boehmite.

Preferably, the supported active material phase is formed while the precursor to the active material phase is in intimate contact with the surface of the support phase particles and the active material precursor is rapidly reacted on the surface of the support phase particles. The reaction and formation of the supported active material preferably occurs over a very short period of time such that the growth of large active material clusters is limited. Preferably, the active material precursor is exposed to the elevated reaction temperature to form the active material for not more than about 600 seconds, more preferably not more than about 100 seconds and even more preferably not more than about 10 seconds. The means by which the active material precursor is reacted is discussed in detail below.

Preferably, the spray processing methods are capable of simultaneously forming a spherical particle structure. The spherical particles form as a result of the formation and drying of the precursor droplets during spray processing.

Spray processing methods for the production of the active materials can be grouped by reference to several different attributes of the apparatus used to carry out the method. These attributes include: the main gas flow direction (vertical or horizontal); the type of atomizer (submerged ultrasonic, ultrasonic nozzle, two-fluid nozzle, single nozzle pressurized fluid); the type of gas flow (e.g., laminar with no mixing, turbulent with no mixing, co-current of droplets and hot gas, countercurrent of droplets and gas or mixed flow); the type of heating (e.g., hot wall system, hot gas introduction, combined hot gas and hot wall, plasma or flame); and the type of powder collection system (e.g., cyclone, bag house, electrostatic or settling).

For example, absorbent and catalytic powders of the present invention can be prepared by starting with an aqueous-based precursor liquid consisting of a dissolved metal salt. The processing temperature of the precursor droplets can be controlled so the metal salt precursor decomposes to form the active material or a solid precursor to the active material.

The first step in the process is the evaporation of the solvent (typically water) as the droplet is heated resulting in a particle of dried solids and/or metal salts. A number of methods to deliver heat to the particle are possible: horizontal hot-wall tubular reactors, spray dryer and vertical tubular reactors can be used, as well as plasma, flame and laser reactors. As the particles experience either higher temperature or longer time at a specific temperature, the metal precursor decomposes. Preferably, the time that the droplets/particles experience a given temperature can be controlled and therefore the degree of porosity, crystallinity, the microstructure and other properties can also be controlled.

The atomization technique for generating the precursor droplets has a significant influence over the characteristics of the final active material powder, such as the particle surface area, porosity, size, the spread of the particle size distribution (PSD), as well as the production rate of the powder. In extreme cases, some techniques cannot atomize fluids with even moderate particle loadings or high viscosities. Several methods exist for the atomization of precursor compositions, including those that contain suspended particulates. These methods include but are not limited to: ultrasonic transducers (usually at a frequency of 1-3 MHz); ultrasonic nozzles (usually at a frequency of 10-150 KHz); rotary atomizers; two-fluid nozzles; and pressure atomizers.

Ultrasonic transducers are generally submerged in a liquid and the ultrasonic energy produces atomized droplets on the surface of the liquid. Two basic ultrasonic transducer disc configurations, planar and point source can be used. Deeper fluid levels can be atomized using a point source configuration since the energy is focused at a point that is some distance above the surface of the transducer. The scale-up of submerged ultrasonic transducers can be accomplished by placing a large number of ultrasonic transducers in an array. Such a system is illustrated in U.S. Patent No.

6,338,809 by Hampden-Smith et al., the disclosure of which is incorporated herein by reference in its entirety.

Scale-up of nozzle systems can be accomplished by either selecting a nozzle with a larger capacity or by increasing the number of nozzles used in parallel. Typically, the droplets produced by nozzles are larger than those produced by ultrasonic transducers. Particle size is also dependent on the gas flow rate. For a fixed liquid flow rate, an increased airflow decreases the average droplet size and a decreased airflow increases the average droplet size. It is difficult to change droplet size without varying the liquid or airflow rates. However, two-fluid nozzles have the ability to process larger volumes of liquid per unit time than ultrasonic transducers.

Ultrasonic spray nozzles also use high frequency energy to atomize a fluid. Ultrasonic spray nozzles have some advantages over single or two-fluid nozzles such as the low velocity of the spray leaving the nozzle and lack of associated gas flow. The nozzles are available with various orifice sizes and orifice diameters that allow the system to be scaled for the desired production capacity. In general, higher frequency nozzles are physically smaller, produce smaller droplets, and have a lower flow capacity than nozzles that operate at lower frequencies. A drawback of ultrasonic nozzle systems is that scaling up the process by increasing the nozzle size increases the average particle size. If a particular particle size is required, then the maximum production rate per nozzle is set. If the desired production rate exceeds the maximum production rate of the nozzle, additional nozzles or additional production units are required to achieve the desired production rate.

The shape of the atomizing surface determines the shape and spread of the spray pattern. Conical, microspray and flat atomizing surface shapes are available. The conical atomizing surface provides the greatest atomizing capability and has a large spray envelope. The flat atomizing surface provides almost as much flow as the conical surface but limits the overall diameter of the spray. The microspray atomizing surface is for very low flow rates where narrow spray patterns are needed. These nozzles are preferred for configurations where minimal gas flow is required in association with the droplets.

Particulate suspensions in the precursor solution (e.g., for the production of a supported active material) may present several problems with respect to atomization. For example, submerged ultrasonic atomizers re-circulate the suspension through the generation chamber and the suspension concentrates over time. Further, some fraction of the liquid atomizes without carrying the suspended particulates. Other problems encountered when using submerged ultrasonic transducers is that the transducer discs can become coated with the particles and or precursor over time. Further, the generation rate of particulate suspensions can be very low using submerged ultrasonic transducer discs. This is due in part to energy being absorbed or reflected by the suspended particles.

For spray drying, the aerosol can be generated using three basic methods. These methods differ in the type of energy used to break the liquid masses into small droplets. Rotary atomizers (utilization of centrifugal energy) make use of spinning liquid droplets off of a rotating wheel or disc. Rotary atomizers are useful for co-current production of droplets in the range of $20\text{ }\mu\text{m}$ to $150\text{ }\mu\text{m}$ in diameter. Pressure nozzles (utilization of pressure energy) generate droplets by passing a fluid under high pressure through an orifice. These can be used for both co-current and mixed-flow reactor configurations and typically produce droplets in the range of $50\text{ }\mu\text{m}$ to $300\text{ }\mu\text{m}$. Multiple fluid nozzles such as a two-fluid nozzle (utilization of kinetic energy) produce droplets by passing a relatively slow moving fluid through an orifice while shearing the fluid stream with a relatively fast moving gas stream. As with pressure nozzles, multiple fluid nozzles can be used with both co-current and mixed-flow spray dryer configurations. This type of nozzle can typically produce droplets in the size range of $5\text{ }\mu\text{m}$ to $200\text{ }\mu\text{m}$.

For example, two-fluid nozzles are used to produce aerosol sprays in many commercial applications, typically in conjunction with spray drying processes. In a two-fluid nozzle, a low-velocity liquid stream encounters a high-velocity gas stream that generates high shear forces to accomplish atomization of the liquid. A direct result of this interaction is that the droplet size characteristics of the aerosol are dependent on the relative mass flow rates of the liquid precursor and nozzle gas stream. The velocity of the droplets as they leave the generation zone can be quite large which may lead to unacceptable losses due to impaction. The aerosol also leaves the nozzle in a

characteristic pattern, typically a flat fan, and this may require that the dimensions of the reactor be sufficiently large to prevent unwanted losses on the walls of the system.

Thus, numerous atomization techniques for spray processing are possible for the production of active material powders and different versions are preferred for different feed streams and products.

The atomized precursor composition must be heated to remove solvents and react precursor components. For example, a horizontal, tubular hot-wall reactor can be used to heat a gas stream to a desired temperature. Energy is delivered to the system by maintaining a fixed boundary temperature at the wall of the reactor and the maximum temperature of the gas is the wall temperature. Heat transfer within a hot wall reactor occurs through the bulk of the gas. Buoyant forces that occur naturally in horizontal hot wall reactors aid this transfer. The mixing also helps to improve the radial homogeneity of the gas stream. Passive or active mixing of the gas can also increase the heat transfer rate. The maximum temperature and the heating rate can be controlled independent of the inlet stream with small changes in residence time. The heating rate of the inlet stream can also be controlled using a multi-zone furnace.

The use of a horizontal hot-wall reactor according to the present invention is generally preferred to produce particles with a size of not greater than about 5 μm . Above about 5 μm , settling of particles can cause significant material losses. One disadvantage of such reactors is the poor ability to atomize particulates when using submerged ultrasonics for atomization.

Alternatively, the horizontal hot-wall reactor can be used with a two-fluid nozzle to atomize the droplets. This approach is preferred for precursor feed streams containing higher levels of particulate materials, such as a particulate support precursor. A horizontal hot-wall reactor can also be used with ultrasonic nozzle atomization techniques. This allows atomization of precursor containing particulates, however the large droplet size leads to losses of materials on reactor walls and other surfaces making this an expensive method for powder production.

While horizontal hot-wall reactors are specifically useful for some particle morphologies and compositions according to the present invention, particularly for the spray pyrolysis method illustrated in Fig. 1, spray processing systems in the

configuration of a spray dryer are the preferred production method for large quantities of absorbent and catalytic powders in accordance with some applications of the present invention. Such spray processing systems are particularly useful for the method schematically illustrated in Fig. 2.

5 Spray drying is a process wherein powders are produced by atomizing a precursor to produce droplets and evaporating the liquid to produce a dry aerosol, wherein thermal decomposition of one or more precursors may take place to produce the powder. The residence time in the spray dryer is the average time the process gas spends in the drying vessel as calculated by the vessel volume divided by the process
10 gas flow using the outlet gas conditions. The peak excursion temperature (i.e., the reaction temperature) in the spray dryer is the maximum temperature of a particle, averaged throughout its diameter, while the particle is being processed and/or dried. The droplets are heated by supplying a pre-heated carrier gas.

 Three types of spray dryer systems are useful for the spray drying of the active
15 material powders according to the present invention. An open system is useful for spray drying of powders using air as an aerosol carrier gas and an aqueous feed solution as a precursor. A closed system is useful for spray drying of powders using an aerosol carrier gas other than air. A closed system is also useful when using a non-aqueous or a semi-non-aqueous solution as a precursor. A semi-closed system,
20 including a self-inertizing system, is useful for spray drying of powders that require an inert atmosphere and/or precursors that are potentially flammable.

 Two spray dryer designs are particularly useful for the production of the active material powders of the present invention. A co-current spray dryer is useful for the production of materials that are sensitive to high temperature excursions (e.g., greater
25 than about 350°C) or that require a rotary atomizer to generate the aerosol. Mixed-flow spray dryers are useful for producing materials that require relatively high temperature excursions (e.g., greater than about 350°C) or require turbulent mixing forces.

 In a co-current spray dryer, the hot gas is introduced at the top of the unit where the droplets are generated with any of the atomization techniques mentioned above.
30 The maximum temperature that a droplet/particle is exposed to in a co-current spray dryer is the temperature of the outlet. Typically, the outlet temperature is limited to

about 200°C, although some designs allow for higher temperatures. In addition, since the particles experience the lowest temperature in the beginning of the time-temperature curve and the highest temperature at the end, the possibility of precursor surface diffusion and agglomeration is high.

5 A preferred spray processing system is based on a mixed-flow spray dryer. A mixed-flow spray dryer introduces the hot gas at the top of the unit and the precursor droplets are generated near the bottom and are directed upwardly. The droplets/particles are forced towards the top of the unit then fall and flow back down with the gas, increasing the residence time in the spray dryer. The temperature the
10 particles experience is also higher as compared to a co-current spray dryer. This is important, as most spray dryers are not capable of reaching the higher temperatures that are required for the conversion of some precursor salts.

For mixed flow spray dryers the reaction temperatures can be high enough for the decomposition of metal precursors such as Rh precursors (e.g., between 250°C and
15 350°C) useful for preparation of reforming catalysts such as a Rh/Al₂O₃ supported catalyst. The highest temperature in these spray dryers is the inlet temperature (e.g., 600°C and higher), and the outlet temperature can be as low as 90°C. Therefore, the particles reach the highest temperature for a relatively short time, which advantageously reduces precursor migration or surface diffusion. This spike of high temperature quickly
20 converts the precursor and is followed by a mild quench since the spray dryer temperature quickly decreases after the maximum temperature is achieved. The spike-like temperature profile is advantageous for the generation of highly dispersed metal or metal oxide active material clusters on the surface of a support phase.

The range of useful residence times for producing the active material powders
25 depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid inlet temperature and the residual moisture content. In general, residence times for the production of the active material powders can range from 5 seconds up to 5 minutes. According to one embodiment, the residence time is from about 15 seconds to about 45 seconds.

The range of inlet temperatures for producing the active material powders depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid, and energy required to perform drying and/or decomposition functions.

5 In general, the outlet temperature of the spray dryer determines the residual moisture content of the powder. For the production of the absorbent and catalytic powders according to the present invention, the range of useful outlet temperatures depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid, inlet temperature, and residual moisture content. For example, a useful outlet temperature according to one embodiment of the present invention ranges from about
10 200°C to about 350°C.

Other equipment that is desirable for producing the active material powders using a spray dryer includes a heater for the gas and a collection system. Either direct heating or indirect heating, including burning fuel, heating electrically, liquid-phase heating or steam heating, can accomplish heating of the gas. The most useful type of
15 heating for the production of the powders processed with an inlet temperature greater than 350°C is direct fuel burning.

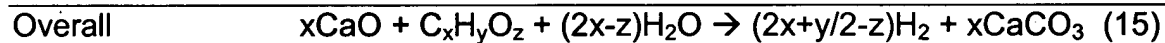
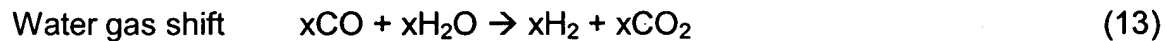
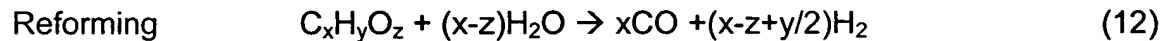
Many collection methods are useful for collecting powders produced on a spray dryer. These methods include, but are not limited to those using cyclone, bag/cartridge filter, electrostatic precipitator, and various wet collection techniques.

20 The powders may also need to be post-processed by conventional calcination methods to convert them into another chemical composition prior to pelletization. For example, it may be advantageous to convert a metal oxalate with a particular structure into a metal carbonate and/or further to a metal oxide through a thermal post-processing step (Fig. 3). Likewise, it may be advantageous to convert a metal carbonate to a metal
25 oxide while retaining the beneficial attributes of the pore structure. The post process ideally needs to be carried out under conditions that are not detrimental to the structure and performance of the material. Where the post processing is a thermally-induced transformation, the temperature needs to be carefully chosen to effect the chemical change, without inducing significant sintering or significantly altering the performance of
30 the material. A number of methods can be used to effect this thermal transformation including heat treatment in a static bed or a moving bed.

One preferred embodiment of the post-processing in a moving bed is the use of a rotary calciner in which the powder is delivered to a furnace which contains a rotating reactor tube such that the bed of particles is constantly moving to avoid particle to particle agglomeration and also provide a fresh exposure of the surface of the particle bed to allow out gassing of the material (CO₂ in the case of the examples described above). This continual "agitation" of the powder bed avoids depth-dependant variations in the sample that can occur with a fixed bed reactor.

AER

The particulate materials of the present invention are particularly applicable to AER processes. As is discussed above, AER has significant advantages over conventional reforming technologies such as conventional steam-methane reforming (SMR), autothermal reforming (ATR) and partial oxidation (POX). The fuels that can be used in AER processes include natural gas, other gases such as propane, liquids such as alcohols, gasoline, diesel and jet fuel, and solid fuels such as biomass, coal and other forms of carbon. A general AER method for hydrogen production using various fuels is illustrated by the reactions of Equations 12 to 15:



where $C_xH_yO_z$ represents different types of carbon-based fuels. For example, when $z \neq 0$, $C_xH_yO_z$ can represent either alcohols such as methanol (CH₃OH), ethanol (C₂H₅OH) or bio-oil from biomass such as dextrose (C₆H₁₂O₆). When $z=0$, C_xH_y represents fossil-based hydrocarbon fuels such as natural gas (predominately methane), gasoline, jet fuel, diesel fuel, and the like. When $y=z=0$, or $z=0$ and $x \gg y$, C_xH_y represents carbon sources such as coal. The benefits of AER compared to conventional steam reformation are illustrated in Table 1 for a number of different gaseous, liquid and bio-fuels. Specifically, Table 1 illustrates the reformate

compositions from conventional steam reforming and AER, calculated based on thermodynamics, for different fuels. These fuels include gasoline (isooctane) and diesel (n-tetradecane). The major chemicals in bio-oil are acids (acetic acid), carbohydrates (dextrose) and oxygenated aromatics (cresol). the temperatures listed in Table 1 are all

5 in °C.

Table 1

<u>Fuel Type</u>	<u>Gas</u>		<u>Liquid Fuel</u>			<u>Bio-oil</u>	
	<u>Methane</u>	<u>Ethanol</u>	<u>Gasoline</u>	<u>Diesel</u>	<u>Acids</u>	<u>Carbohydrates</u>	<u>Aromatics</u>
Conventional steam reforming (SR)							
Temperature	730	659	708	708	610	610	659
H ₂	77.04	71.35	71.84	71.57	62.54	62.54	66.05
CH ₄	0.32	0.86	0.41	0.40	0.99	0.99	0.85
CO	13.56	16.67	14.44	14.50	8.35	8.35	12.98
CO ²	9.08	11.12	13.31	13.53	28.13	28.13	20.12
Absorption-enhanced reforming (AER)							
Temperature	610	513	610	600	513	513	561
H ₂	98.84	99.05	99.10	99.14	99.69	99.69	99.40
CH ₄	0.82	0.93	0.57	0.61	0.29	0.29	0.52
CO	0.22	0.01	0.19	0.14	0.01	0.01	0.04
CO ₂	0.13	0.01	0.11	0.10	0.01	0.01	0.04
Reforming Catalysts							
	Rh/Al ₂ O ₃	Co,M/M' _x O _y	M/M' _x O _y -Al ₂ O ₃	M/M' _x O _y -Al ₂ O ₃			
	M=Rh, Ru, Pt, Pd, alloys; M<1.5%						
	M' _x O _y =CeO ₂ , ZrO ₂ , Ln ₂ O ₃ (where Ln=lanthanide group metal), SiO ₂ , MgO, ZnO, TiO ₂						

5 Figs. 4 and 5 illustrate the calculated thermodynamic gas composition (dry basis) obtained by steam methane reforming (SMR) as a function temperature at atmospheric pressure with and without a CaO absorbent. Specifically, Fig. 4 illustrates that at 600°C, AER can achieve at least 98% conversion to H₂, as compared to only 75% conversion under normal conditions of SMR, as illustrated in Fig. 5. Further, Fig. 4

10 illustrates that the CO concentration can be decreased to less than 1% in an AER reformer as compared to the normal of 6 to 10% in conventional SMR, and the total amount of carbon oxides including CO and CO₂ is less than 2%, as compared to 25% in conventional SMR (Fig. 5). Similar conclusions can be reached by comparison of SMR and AER thermodynamics for reforming of other fuels such as LPG, gasoline, kerosene,

15 jet fuel, bio-oil from biomass and carbon (see Table 1). Therefore, for a variety of fuels, it is desirable to remove the CO₂ during the reforming step as opposed to post WGS CO₂ removal.

Table 2 illustrates a comparison of the various features of natural gas steam reforming (SMR), auto-thermal reforming (ATR) and absorption-enhanced reforming (AER).

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Table 2

	Reforming Type		
	SMR	ATR	AER
Reaction	$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	$\text{CH}_4 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2$	$\text{CaO} + \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 4\text{H}_2$
Reforming Conditions	~800°C	>750°C	600°C
Sulfur Removal	Yes	Yes	Yes
Reforming Catalyst	Yes	Yes	Integrated with CO ₂ absorbent
Reformate Composition	~75% H ₂ >20% CO + CO ₂ ~1% CH ₄	~75% H ₂ >20% CO + CO ₂ ~1% CH ₄ N ₂	~98% H ₂ <1% CO + CO ₂ <1% CH ₄
WGS Catalyst: High Temperature Low Temperature	Yes Yes	Yes Yes	No specific demand No
CO Cleanup	PrOX	PrOX	Methanation
H₂ Purification	PSA or membrane	PSA or membrane	None required
Steps for >98% H₂	SR, WGS, PrOX, PSA	ATR, WGS, PrOX, PSA	AER and methanation
BOP Materials Requirement	Medium	High	Relatively low
Overall H₂ Efficiency	~75%	~75%	~100%

In addition to AER, absorbents such as CaO are used in a variety of other applications to remove poisons, contaminants or reaction by-products. The compounds to be removed are normally gases under the operating conditions of the system and the absorbents are usually heated to elevated temperatures in order to initiate a chemical reaction between the gas to be removed and the surface of the absorbent. The chemical reactions between the absorbent and the gas to be removed are normally stoichiometric, so once the active material in the absorbent has either been consumed or rendered passive it is either physically replaced or the material is isolated and the reaction is reversed to re-generate the original material

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For example, H_2S can be removed from a gas stream using CaO as the absorbent to react with the H_2S to form calcium sulfide (CaS). The CaO absorbent can be regenerated from the CaS bed by oxidation-reduction reactions as illustrated by Equations 8 to 11.

5 A simple illustration of one cycle of carbonation/decarbonation of CaO with CO_2 is illustrated in Fig. 6. Referring to Fig. 6, an activated absorbent bed comprising CaO is packed into a reactor. The absorbent bed can include loose CaO powder, pelletized CaO powder or a surface coated with CaO powder. A gas stream including CO_2 is admitted to the reactor and the CaO reacts selectively with the CO_2 to form CaCO_3 .
10 Further reaction between the CaO and CO_2 eventually consumes all the available CaO and converts it into CaCO_3 , which is non-reactive with CO_2 . Further use of this reactor under these conditions will not remove additional CO_2 and the contaminated gas will pass through the reactor. The feed is then stopped and a regeneration gas, in this case air and water, is passed through the reactor, which is heated to an elevated
15 temperature, to reverse the reaction, remove CO_2 from the CaCO_3 and thereby regenerate the active CaO absorbent bed. While CaO is described as an example of a reversible CO_2 absorbent throughout the body of this text, those skilled in the art will recognize that there are a number of other materials to which the same principles of this invention also apply. These absorbent materials can include the oxides of Group IA and
20 Group IIA metals of the periodic table of elements.

Despite the theoretical improvement offered by AER, it has not been widely implemented. One of the major barriers to the implementation of AER has been the need for a CO_2 absorbent with high performance (CO_2 absorption capacity) that does not degrade significantly over the number of cycles (generation of H_2 followed by
25 regeneration of the CO_2 absorbent) that are required for a commercial product. That is, after CO_2 absorption, the absorbent must be regenerated, or decarbonized, to remove the absorbed CO_2 . Currently available absorbent materials start to degrade in performance over just a few cycles and cannot retain high constant capacity during subsequent cycles, and therefore are not commercially useful.

30 The primary issue affecting recyclability is that CaCO_3 has a much lower density than the CaO absorbent. Therefore, for a fixed mass of absorbent in a reactor bed,

there is a large volume increase as CaO is converted to CaCO₃. Due to the high temperature typically required for cycling the CaCO₃ back to CaO, particle sintering and reduction of porosity occurs leading to a reduced CO₂ absorption capacity on the second cycle. Therefore, a high initial absorption capacity through the production of a high surface area CaO powder will not, by itself, lead to retention of a high capacity during subsequent cycles. Decrepitation is also common and leads to plugging of the bed.

In the context of the cyclic nature of AER, both the kinetics and the mechanism of the carbonation and decarbonation reactions are important. In order to achieve a high absorption capacity, it is necessary to use a material having a high content of active absorbent compound, such as CaO. However, a number of design criteria need to be taken into account involving the chemical, physical and system aspects of the reversible CO₂ reaction bed. These aspects include the careful design of the microstructure of the material to decrease diffusion-based limitations associated with gas transport and surface diffusion through the substantially impervious CaCO₃ surface layer, the chemical composition and microstructure to adjust the rate constants of the carbonation/decarbonation reactions and the strength of the material in pelletized and/or coated form. As is discussed above, one of the critical issues to overcome is the change in density and therefore microstructure and porosity on cycling between CaO and CaCO₃.

Current reactive CO₂ absorbents suffer from a rapid loss of porosity and from sintering during multiple carbonation/decarbonation temperature swing operations. The materials prepared by conventional methods, such as precipitation and solid state processing, either lack the desired porosity or the desired crystal size, which are two critical parameters to material performance. An absorbent lacking adequate porosity will result in slow kinetics for both carbonation and decarbonation. Some research suggests that an average pore size in the range of 5 to 20 nm is less susceptible to pore plugging. (Ghosh-Dastidar, A.; Mahuli, S. K.; Agnihotri, R.; Fan, L.-S. Investigation of High Reactivity Calcium Carbonate Sorbent for Enhanced SO₂ Removal. *Ind. Eng. Chem. Res.*, 1996, 35 (2), 598). Also, CO₂ gas can only penetrate a thin (about 0.1 μ m) shell of the CaO solid particle during repeated carbonation and decarbonation cycles,

which is less than one tenth of the normal CaO particle size. CO₂ absorbents present in natural and conventional materials generally have a large particle size, low porosity and do not have a three-dimensional pore network structure.

According to one embodiment of the present invention, the microstructure of the absorbent particles is controlled to enable mass transport of the reactants and products to and from the surface of the powder during contaminant removal and regeneration and to retain the beneficial microstructure throughout multiple cycles. The absorbent particles according to this embodiment are produced by spray processing, which enables tight control over the chemical composition and microstructure of the materials.

The powder batch produced by spray processing according to one embodiment of the invention includes substantially spherical aggregates of smaller particles. This particle structure is illustrated in Fig. 7. The spherical aggregates may have different sizes and spread of size distribution that can be controlled by the spray processing manufacturing process. The microstructure of the aggregates is also controlled by the spray processing process to control the surface area, crystallinity, size and porosity within each aggregate. The aggregate microstructure, average size and spread of the size distribution are controlled to provide the optimum performance in a given application depending on the operating and regeneration parameters. In another embodiment of the invention the substantially spherical particles are composite particles that have controlled composition and morphology (Fig. 8). For example, the particles can include various ratios of CaO and MgO or Al₂O₃, with other metals or metal oxides present to achieve desired catalytic properties such as enhanced adsorption kinetics, water-gas-shift activity or reforming activity. The role of additives that are inert with respect to CO₂ absorption such as MgO or Al₂O₃ is to aid the recyclability of the CaO containing powders by minimizing the sintering and loss of surface area and pore volume. The sintering inhibition characteristics of these additives may be derived from the composite nature of the microstructure and/or from the use of dopant ions in the CaO lattice. The d₅₀ average particle size of the absorbent powders generated by spray conversion methods (the intermediate compounds, or the final compositions such as calcium carbonate or calcium oxide) is preferably not greater than 20 μm, more preferably not greater than 10 μm and even more preferably not greater than 5 μm.

The surface area of the aggregate or composite absorbent powders will depend on the composition (addition of inert compounds such as alumina); however the surface area (as measured by BET nitrogen adsorption) is preferably greater than 5 m²/g, more preferably greater than 10 m²/g, even more preferably greater than 15 m²/g and most preferably greater than 30 m²/g.

The pore volume of the absorbent powders generated by spray processing methods according to the present invention (the intermediate compounds, or the final compositions such as calcium carbonate or calcium oxide) is preferably greater than about 0.01 cm³/g, more preferably greater than about 0.04 cm³/g and even more preferably greater than about 0.15 cm³/g. In one embodiment, the pore volume is from about 0.05 cm³/g to about 0.3 cm³/g. As is discussed above, the pore volume of the absorbent powder can be increased by including a pore enhancing agent in the precursor composition. Further, the absorbent (e.g., CaO) can advantageously absorb CO₂ to form a carbonated absorbent compound (e.g., CaCO₃) where the pore volume of the carbonated compound is not less than 70% of the pore volume of the absorbent compound, more preferably is not less than 80% of the pore volume of the absorbent compound and even more preferably is not less than 90% of the pore volume of the absorbent compound.

Spray processing enables control over the powder batch characteristics in the following manner. The aggregate size and spread of the aggregate size distribution is controlled by controlling the size and size distribution of the droplets produced by the droplet generator because each individual droplet becomes an individual particle. The size and size distribution of the aggregates in the powder batch is controlled independent of the chemical composition of the powder. Furthermore, the microstructure, composition and crystallinity of the aggregates and the sub-particles that comprise the aggregates are controlled by the nature of the precursors that are used to produce the droplets and the processing parameters (especially the temperature/time history) of the particles in the gas phase during spray processing. As a result, the powder batch produced by spray processing, whether directly used to produce pellets or powder coatings, or used after post-processing subsequent to the spray processing step, can have a controlled microstructure at a number of different length scales. The

size and size distribution of the particles produced by spray processing can be varied to control the pore size and size distribution between the aggregates (inter-aggregate porosity, Fig. 7).

The aggregates produced by spray processing according to the present invention are preferably in the size range of from about 0.3 μm to about 20 μm . As a result, the pore sizes of the inter-aggregate pores will typically be in the micron size range and therefore classified as macroporosity. In one embodiment of the present invention, the aggregates are composed of finer sub-particles of the absorbent material that have been aggregated through the spray processing method. The finer sub-particles are derived either from soluble reagents or suspensions of reagents. The typical size of the sub-particles is in the range of from about 30 nm to 1000 nm. As a result, the size of the pores formed between the sub-particles in the aggregate are in a similar size range (30 nm to 1000 nm) and are classified as mesoporosity. Finally, the sub-particles themselves can range from being fully crystalline (i.e., single crystal) to being amorphous. Single crystal sub-particles are likely to be fully dense and exhibit no further porosity, but amorphous particles can include pores that are classified as microporosity. In another embodiment of the present invention, the absorbent particles are composite particles of various amorphous or crystalline metal oxides.

The correct combination of macroporosity, mesoporosity and microporosity will depend on the composition of the material, the conditions under which it is reacted with the species to be absorbed and the conditions under which the de-activated absorbent is re-activated. The importance of this aspect of the invention can be clarified further by reference to specific materials. Table 3 lists the density of a number of relevant Ca-based compositions and the calculated volume per mol of fully dense material.

Table 3

Compound	Density (g/cc)	Volume (cc/mol)
CaO	3.25	17
CaCO ₃	2.93	37
CaS	2.5	29
CaC ₂ O ₄	2.2	67

The density of the CaCO_3 is lower than that of CaO as expected from the higher atomic volume of CO_2 . As a result, given that the molar mass of calcium is constant through the removal of CO_2 and the reactivation of the CaCO_3 , the volume will increase on conversion of the CaO to CaCO_3 . Therefore, this volume increase is likely to remove some of the porosity imparted to the original CaO powder. Regeneration of CaO from CaCO_3 will result in a decrease in volume of the absorbent, but the pore structure formed as a result of the regeneration of CaO could be significantly different relative to the starting CaO . This is typically the problem with existing CaO powder made by conventional routes because the majority of the reactivity is derived from the high surface area of small particles and/or the presence of a roughened surface. After several regeneration cycles, the surfaces become smooth and/or the small particles tend to sinter, leading to a reduction in surface area and pore volume, and a reduction in reactivity. According to one embodiment of the present invention, the porosity of the absorbent powder batch is controlled at the microporosity, mesoporosity and macroporosity scales to reduce the loss of surface area and pore volume and maintain a high activity over a large number of regeneration cycles. In one embodiment of the present invention, the aggregate particles formed by the spray processing method have controllable inter-aggregate porosity (i.e., porosity between the aggregates) as well as intra-aggregate porosity (i.e., porosity within the aggregates). Clearly, it would normally be expected that the inter-aggregate pores (micron size) are larger than the intra-aggregate pores (nanometer size).

In some cases, the absorbent reacts with species to be removed on the surface of the absorbent and forms a passivating layer, which limits the further reaction of underlying absorbent with the contaminant. As a result, the mass activity of the absorbent is relatively low and once the surface of the absorbent has reacted with the contaminant species, no further reaction with the contaminant can occur. One way to improve the mass activity according to the present invention is to disperse the absorbent on or form a composite with a relatively high surface area support, which is passive or inert (i.e., does not substantially react) with respect to the contaminant. A representation of this embodiment is illustrated in Fig. 9, where the spray-processed spherical agglomerates include sub-particles made up of support material with an

absorbent supported/dispersed over the surface of the sub-particles. The methods for controlling the microstructure and morphology of the absorbent powder, as described above, can also be applied to the supported absorbent. The structure of the supported absorbent material can be in the form of a coating around the support particles or as a composite with interpenetrating support and absorbent material networks.

There are a number of advantages in accordance with this embodiment of the invention. The mass activity of the absorbent is significantly higher compared to the situation where an unsupported absorbent is used, assuming that the surface of the unsupported absorbent passivates. This can enable the use of more exotic or expensive absorbent materials, because a relatively small mass of absorbent can be dispersed over the surface of or inter-mixed with a relatively inexpensive support such as silica (SiO_2) or alumina (Al_2O_3). The presence of inert materials can isolate the active component and prevent sintering of the material, particularly during multiple temperature swings and cycles. A further advantage is that the support does not substantially react with the contaminant species and therefore there is no change in the volume or density of the support framework. As a result, the microstructure of the powder does not change significantly and a relatively high surface area can be preserved over a large number of regeneration cycles. The specific microstructure of the supported or composite absorbent will depend upon the specific reaction needs. For example, a relatively thin coating of a highly reactive supported absorbent may have extremely good selectivity and reactivity to remove low levels of gas species at a relatively high space velocity. However, the capacity of the absorbent bed will be relatively low due to the relatively low mass of absorbent present compared to a thicker coating. As a result, a larger bed may be required to increase the total capacity of the absorbent. Alternatively, a thicker absorbent coating on an inert support or a composite particle with interpenetrating networks of absorbent and inert materials may require lower space velocities, but the capacity of the bed will be higher. However, there may also be situations in which nano composite structures comprised of relatively high mass of absorbent but with appropriate porosity might enable high space velocities.

According to another embodiment of the present invention, the absorbent materials are fabricated from intermediate calcium compounds having a low density,

such as calcium oxalate (CaC_2O_4) and calcium carbonate (CaCO_3). Decomposition of these intermediate compounds into the CaO absorbent will alter the microstructure of the intermediate compound, but in a controlled way, and will therefore lead to an increased surface area in the CaO absorbent as compared to conventional preparation methods. In addition, the spray processing method for making either the intermediate compound or the final absorbent compound introduces additional levels of meso and micro porosity and therefore a specific microstructure which is unattainable with conventional preparation methods.

According to this embodiment, the microstructural changes to the absorbent that occur during regeneration cycles is reduced by starting with a powder batch that includes an intermediate composition that has a density similar to or less than that of the reacted absorbent, but which itself is a precursor to form the absorbent material. The goal is to establish the microstructure of the powder using a low density intermediate material to avoid sintering of the particles and reduction in surface area and porosity. One approach is to produce the reacted material as the intermediate powder batch, for example a powder batch including CaCO_3 , rather than only CaO. After the powder batch including CaCO_3 is pelletized or coated onto a surface, the CaCO_3 is treated to form CaO having a high level of porosity. Controlling the microstructure of the CaCO_3 powder batch establishes the specific microstructure, surface area and porosity in the system with a combination of composition (addition of inert additives) and processing conditions (choosing correct spray conversion and post processing conditions) for the absorbent material. When CaO is formed from CaCO_3 in the first step, because CaCO_3 has a lower density than CaO, the surface area and porosity of the CaO batch will decrease to a lesser extent relative to the CaCO_3 batch from which it is derived if a beneficial starting porosity structure is achieved in the initial intermediate compound.

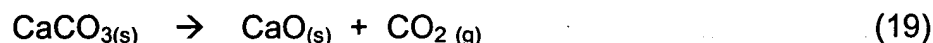
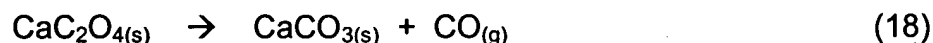
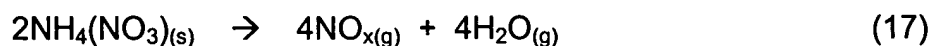
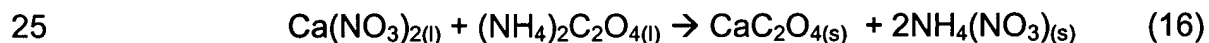
Other materials with a low density can be selected as the intermediate material. Referring to Table 3, calcium oxalate (CaC_2O_4) has a lower density than CaCO_3 . Therefore, CaC_2O_4 can be used as a starting material to establish the microstructure, porosity, aggregate size and size distribution of the powder batch. A wide variety of other materials can also be used which have a density similar to CaCO_3 , in particular

inorganic and metal-organic compounds which are soluble in water or other solvents such that they can be employed in spray processing.

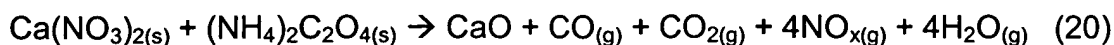
This embodiment of the present invention is illustrated in Fig. 10. In the first step, after forming the pellet or depositing the powder coating including the low density material, the powder batch is treated to form the activated absorbent in a form that has a higher surface area and porosity compared to the starting material. The powder batch can be treated either before pelletizing or coating by post-processing of the intermediate compound powder or after pelletizing or coating the intermediate powder into the reactor. The activated absorbent is then used to remove the contaminant species and is converted to the deactivated absorbent. The deactivated absorbent will have the pore distribution and microstructure capable of sustaining multiple generation cycles without significant loss of surface area, porosity or structural integrity.

The reversible reaction with CO₂ is less likely to close porosity and reduce the surface area of CaO obtained by direct spray processing or post processing through the sequential decomposition of CaC₂O₄ or CaCO₃ as compared to designing the microstructure around CaO. Another aspect of this embodiment of the present invention involves the execution of sequential chemical reactions involving specific reagents and pore forming chemicals performed by spray processing to produce discrete particles comprising specific compositions and microstructures that are constructed in a logical design sequence. This aspect of the present invention is illustrated in Fig. 2.

Specifically, Fig. 2 illustrates a case where the chemical reactions in the individual particles occur in the following sequence:



Leading to the overall chemical reaction:



By carrying out this reaction in a stepwise fashion in the gas phase, the microstructure can be fabricated in a stepwise fashion. This ability does not exist in a single solid-state or liquid phase powder manufacturing step.

The precursors and reagents are chosen with the intent to lead to the following reaction sequence. Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is one preferred precursor for CaO in spray processing methods such as spray pyrolysis and spray conversion. In this reaction sequence the evaporation of water occurs quickly, on the order of milliseconds, while the whole gas phase material processing sequence takes place on the order of seconds. Therefore, the majority of the reactions in this sequence are solid-state reactions. $\text{Ca}(\text{NO}_3)_2$ reacts with $(\text{NH}_4)_2(\text{C}_2\text{O}_4)$ according to the reaction of Equation 16 to form CaC_2O_4 . The reaction rate can be suppressed at room temperature using the correctly formulated (pH adjusted) solution. CaC_2O_4 has a low solubility in water and thermally decomposes before it melts, so the reaction can occur in the solution phase as the droplets enter the reactor and the microstructure of the resulting CaC_2O_4 product is preserved. The NH_4NO_3 that is formed acts as a pore forming reagent and thermally decomposes at a temperature higher than the temperature at which CaC_2O_4 is formed but lower than the decomposition temperature of CaC_2O_4 , thus introducing porosity. CaC_2O_4 is known to thermally decompose first to CaCO_3 (at about 500°C) and then to CaO (at about 750°C). Therefore, in this sequence, the microstructure and porosity designed into the solid-state product is first constructed around CaC_2O_4 , the material with the highest molar volume, and then transferred to CaCO_3 and ultimately to CaO through post-processing steps. The crucial aspect of this reaction scheme is that the reactions occur sequentially, separated by both time in the reactor as well as the temperature at different locations in the reactor while substantially retaining the microstructure at both the nanometer scale and micrometer scale. If the same reagents are processed by conventional solution and/or solid-state processing, the microstructure cannot be tailored across this wide variety of length scales in discrete particles.

It is worth noting that the foregoing embodiments can be employed in any variation or combination to achieve excellent reactivity and the ability to go through

multiple regeneration cycles (recyclability). For example, the ability to control the microstructure, morphology, aggregate size and aggregate size distribution within an absorbent powder batch can be combined with a supported absorbent or with a supported low density precursor to an absorbent. For example, in the case where the powder batch is pelletized, one of the phases can be selected to create a structural support such that during active use and regeneration, the pellets retain their structural integrity. For example, the support on which the precursor to the active absorbent or the active absorbent itself is dispersed can be an active material in peptization during pellet formation to form a three-dimensional support network. In addition, one or more catalytically active materials may be incorporated into the structure to achieve a catalytic function in addition to a gas absorption function. This aspect of the present invention is discussed in more detail below.

According to one embodiment of the present invention, the absorbent material, which includes the CaO absorbent compound, can include a second component that does not undergo the carbonation/decarbonation reaction, such as MgO. Dolomite is a naturally existing material comprised of CaCO_3 and MgCO_3 . However, natural dolomite has fairly low initial surface area and comprises only about 50 wt.% CaCO_3 and therefore the initial capacity is significantly reduced and the change in microstructure on carbonation/decarbonation cycles leads to rapid loss of surface area and porosity. The presence of MgO in processed natural dolomite does introduce some advantageous WGS capability to the material. However, it has been found according to the present invention that other additional components can be used to achieve improved WGS activity at much lower weight loadings, as is described below.

According to one embodiment of the present invention, the recyclability of the CaO absorbent can be improved by integrating the absorbent with substantially inert additional materials such as metal oxides selected from Al_2O_3 , MgO, TiO_2 or SiO_2 to form composite particles. Aluminum oxides and magnesium oxides are particularly preferred. For example, the introduction of soluble reagents such as $\text{Mg}(\text{NO}_3)_2$ in the starting precursor solution will result in the formation of a tailored dolomite-like composition. Introduction of nanophase particulate Al_2O_3 will result in the formation of a CaO/ Al_2O_3 composite. The composition of the intermediate compound as well as for

the final absorbent powder is also of great importance since it determines if the combination of high absorption capacity and excellent recyclability can be achieved. For example, low amounts of the inert additive (alumina, titania, silica or MgO) may lead to absorbent materials that have high sorption capacity since the amount of CaO will be high. However these high CaO materials may not have enough resistance to sintering and may be susceptible to rapid decrease of surface area and porosity, and therefore have low activity after multiple cycles. The amount of inert additive therefore is preferably not greater than 50 wt.% of the total absorbent powder, such as from about 1 wt.% to about 50 wt.%. More preferably, the inert additive is present at a level of not greater than 25 wt.% of the total absorbent powder such as from about 5 wt.% to 25 wt.% and even more preferably is not greater than 15 wt.% of the total absorbent powder. The composite particles can have an average particle size of from about 1 μm to about 50 μm , such as from about 4 μm to about 20 μm . Preferably the composite particles are highly porous and have a pore volume of at least about 0.15 cm^3/g .

The composite absorbent material which includes the absorbent compound and the inert compound can retain a high absorption capacity, such as at least about 10 grams CO_2 per 100 grams of unreacted absorbent material. More preferably, the absorbent material retains an absorption capacity of at least about 20 grams CO_2 , and even more preferably at least about 30 grams CO_2 , per 100 grams of unreacted absorbent material. The absorbent compound contained within the absorbent material preferably has an absorption capacity of at least about 50 mol.%, more preferably at least about 70 mol.% and even more preferably at least about 90 mol.%.

Reaction Rate Enhancement

The reactivity of the individual active sites in the absorbent compound is dictated by the chemical composition and crystalline structure of the absorbent as well as by the reaction conditions during manufacture of the absorbent. The chemical composition can influence the activity for a specific reaction with a gas species by adjusting the electronic and steric nature of the activity of the surface reaction sites. For example, the presence of a dopant can enhance the reactivity compared to the material without a dopant. Steric effects may enhance the reactivity by having atoms present which distort

the surface structure to make the active sites more sterically accessible for reaction with the contaminant. The reactivity of the absorbent is also strongly influenced by its crystalline structure, and surface defects are also known to enhance the reactivity of the surfaces. Different crystal faces of a crystalline material also have different reactivities and crystalline materials with more reactive crystallographic planes exposed on the surface will result in a higher overall activity of the absorbent. In some cases amorphous (non-crystalline) materials are more reactive than crystalline materials. The size of the individual amorphous or crystalline particles can also be important due to the strain when very small particles or crystallites are present, especially below about 50 nm in size.

The number of active sites is also important to the overall activity of the absorbent compound. The total number of active sites normally correlates with the content of the active component and the surface area of the material. An absorbent that has a higher surface area will have a higher number of active sites. The total activity of the material, often defined by its mass activity or specific activity, is the product of the number of active sites and their individual activity. Therefore, the surface area of two samples of the same material may be similar, but because the reactivity of the respective active sites in each material is different, the total reactivity is different. Also, some active sites may be disposed in pore channels that are too small to be reached by the targeted species (e.g., CO₂). Indeed, it is possible to have an absorbent that has a lower surface area relative to another sample of the same material, but that has a higher overall activity. This is why in the design of absorbent materials, other factors such as pore volume and pore size distribution, surface composition and crystallinity of the phases are as important as the surface area with respect to achieving high overall absorption capacity. In addition, the ability of the absorbent structure to retain its pore structure and surface composition after thermal and reaction cycles is critical to its use as a reversible absorbent. In summary, both the concentration (number) of accessible active sites and their individual activity determine the overall reaction kinetics and have a strong influence on the system design and operating conditions.

The recycle time in the fuel processing system is dictated by the size of the CO₂ absorbent bed, the number of beds present and the rate at which the CO₂ is absorbed

and desorbed. Based on the initial studies of the materials and the thermodynamics among CaO, CO₂ and CaCO₃, it has been determined that CO₂ absorption has a relatively high rate at a lower temperature compared to CO₂ desorption, as expected. In addition, provided the microstructure of the materials in the bed is correctly designed and within typical space velocities, it is likely that the methane feed rate, rather than the surface reaction kinetics, limits the rate of carbonation. This assumes that through the optimum microstructure, the formation of an impervious CaCO₃ layer is avoided, which is known to limit the rate of CO₂ uptake after all exposed surfaces of CaO have reacted.

The more difficult problem to solve is achieving decarbonation kinetics that are sufficiently rapid that the decarbonation step does not limit the recycle time. Increasing the temperature can increase the rate constant for the decarbonation reaction, but this may lead to some sintering of the material and reduce the cycle life. Therefore, alternative strategies need to be employed to minimize the time required for decarbonation.

The microstructure of the CaO bed can affect the rate of decarbonation and an increase in the rate of decarbonation has been observed as the particle size of CaO-based powders is decreased. Since the size of the CaO particles is not small enough to introduce changes in the strength of the chemical bonds (i.e., the particles are below a quantum confinement limit of about 30 nm), these results most probably reflect a change in the powder microstructure leading to an improvement in the diffusion transport characteristics of the material. However, the microstructure according to the present invention can also be further optimized to improve the kinetics of the reaction provided the feature size of the changes are at or below a crystallographic length scale of 30 nm (i.e., to create surface tension and surface pressure effects).

According to the present invention, the CaO lattice structure can also be doped with elements that lead to an enhancement of the kinetics of the decarbonation reaction. The dopants can be selected from mono-valent, divalent and polyvalent metals, preferably from the group consisting of Mg, Ni, Zn, Fe and Cu. Preferably, the dopants are present at a level of at least about 0.1 at.% and not greater than about 10 at.%, such as from about 1 at.% to about 5 at.%. These dopants can also lead to an enhancement of the rate of CO₂ absorption by the CaO-based absorbent. Therefore, it

is preferred that the changes in the absorbent composition do not lead to an increase in the rate of decarbonation at the expense of decreasing significantly the rate of absorption and therefore to change the rate-limiting step for carbonation from being limited by the fuel feed to the rate of the surface reaction.

- 5 The doped CO₂ absorbent material retains a high surface area and preferably has a surface area of at least about 5 m²/g, more preferably at least about 10 m²/g, even more preferably at least about 20 m²/g and even more preferably at least about 30 m²/g. Further, the pore volume over the doped particulates can be from about 0.05 cm³/g to about 0.3 cm³/g.
- 10 Accordingly, high performance CO₂ absorbents can be fabricated by spray processing CaO-based absorbents that have varying amounts of metal ions, which have a smaller ionic radius compared to Ca²⁺ and are electropositive so that the presence of such a hetero atom in the structure of CaO will change the physicochemical properties of crystal structure by altering the bond distance and electronic structure owing to the
- 15 difference of ion potential (Z/r) between the calcium ion and the introduced metal ions. Accordingly, Mg, Ni, Zn, Fe and Cu cations are preferred, provided that the doped absorbent materials have a crystal structure similar to CaO with an isometric-hexoctahedra structure and/or similar to dolomite with a trigonal-rhombohedral structure, such as akimotoite and ankerite with a composition of (M_xN_yP_z)CO₃, where M,
- 20 N and P are the divalent or higher valency metal cations other than Ca, such as Mg, Fe or Si and where x, y, z are the molar fraction of total metal ions.

Regeneration of Sample Performance during System Operation

- 25 During reversible absorption of CO₂, the microstructure of the particles can change over longer periods of time at elevated temperature and/or after a large number of cycles. This can lead to a decrease in the absorption capacity of the material. The absorption capacity can be restored by the treatment of the material with reagents that can re-establish the pore structure of the material. One such reagent that can increase the capacity of the absorbent material after it has been reduced is water. Treatment of
- 30 the absorbent with water above room temperature increases the capacity of the material for future cycles. This treatment can be applied multiple times to prolong the material

lifetime (i.e., the capacity and number of cycles of the material). While not wishing to be bound by any theory, it is believed that the mechanism of the performance improvement is as follows. The reduction in capacity is likely due to a sintering of the material at the nanosize level. In the case of CaO, it is likely that the surface area is reduced over time through chemical rearrangement and formation of Ca-O-Ca bonds, possibly via formation of Ca-OH intermediates, removing previously accessible pores. The reaction of the strained Ca-O-Ca bonds with water or another similar reagent, regenerates Ca-OH bonds which on carbonation re-establishes the previous structure.

Other reagents that may be suitable to regenerate the surface area and recyclability of these materials, including protic reagents such as methanol, organic acids and inorganic acids.

SMR Catalysts

Two types of materials are required to affect the overall reaction illustrated by Equation 15, namely a highly reactive, high capacity, highly reversible CO₂ absorbent as is discussed above, and a highly active SMR catalyst to catalyze the reaction of Equation 1. Nickel-based catalysts are often used because they are highly active and inexpensive, but they are susceptible to sulfur poisoning and carbon deposition at steam to carbon molar ratios (H₂O:C) below about 3:1. This can lead to shorter life and reliability of the reforming system.

A variety of catalyst compositions may be valuable to effect catalytic reactions in general and steam reforming reactions in particular. These materials are typically comprised of active catalyst materials dispersed over the surface of a relatively high surface area support. The active catalyst particle is typically a metal, metal alloy, metal oxide, metal nitride or metal carbide and the support phase typically comprises a metal oxide, or in some cases carbon, a metal or a metal nitride. The above materials can be made by a spray processing method as is described above, such as where a precursor to the active phase is dissolved in a solvent, which also contains dispersed particles of the support, and droplets of the suspension are generated and subjected to a heat treatment in various spray processing configurations. Depending on the time-

temperature history, active clusters are formed onto the surface of the high surface area support.

Rh/Al₂O₃ catalysts are preferred according to the present invention since this catalyst is highly active and less sensitive to poisoning by sulfur contaminants than nickel-based SMR catalysts. However, this catalyst contains a relatively expensive precious metal (Rh).

To develop Rh/Al₂O₃ reforming catalysts that are commercially acceptable, the Rh loading on the support must be relatively low while remaining highly active to convert hydrocarbons to H₂ at a level close to the equilibrium level under the reforming conditions, particularly at a high space velocity. The catalyst should also have a sufficient lifetime. According to one embodiment of the present invention, the Rh/Al₂O₃ materials have a high dispersion of Rh on the Al₂O₃, and the Al₂O₃ can be selected to have a range of surface areas and porosities. Such catalysts can be fabricated by spray processing.

According to the present invention, the steam-reforming catalyst includes a support material, preferably a support material selected from the group consisting of the metal oxides of aluminum, cerium, zirconium, lanthanum, silicon, magnesium, zinc and combinations thereof. The support material includes a metal (i.e., metal clusters) dispersed on a support material wherein the metal is preferably selected from the group consisting of rhodium, nickel, ruthenium, platinum, palladium and alloys thereof. Rhodium is particularly preferred. The reforming catalyst preferably includes from about 0.1 wt.% to about 1 wt.% of the metal. A particularly preferred reforming catalyst includes rhodium dispersed upon an alumina support (Rh/Al₂O₃).

The reforming catalyst can also be produced by spray conversion separately or can be incorporated into the CaO absorbent, i.e., as a multi-functional composite material. Fig. 11 illustrates one of the preferred embodiments of this aspect of the present invention where the Rh/Al₂O₃ catalyst is prepared in combination with the CaO absorbent material.

Integration of WGS Catalysts

There are various levels of synergy required between all functions needed to achieve high efficiency in the overall AER reaction. Therefore, in addition to the absorption function, two or more other functions can be integrated. For example, in addition to the reforming activity, materials with WGS activity can also be incorporated to enhance the carbonation/decarbonation kinetics.

Even in the presence of a CO₂ absorbent, steam reforming alone will likely be insufficient to guarantee a low CO content in the reformed fuel stream. As a result, sufficient amounts of high-temperature WGS catalysts can be incorporated into the reformer to ensure rapid conversion of CO to CO₂. For example, the WGS catalyst can be incorporated into the Al₂O₃ support of the Rh/Al₂O₃ particles. The WGS catalyst can also be incorporated into the CaO absorbent. Further, a single composite material can be produced in which the Rh/Al₂O₃ and WGS catalyst can be incorporated onto the surface of the CaO. Two of these embodiments are illustrated in Fig. 11. For reasons of material compatibility within the system, perovskite phase metal oxide catalysts based on Ca are particularly preferred as the support phase.

Other WGS catalyst compositions that can be incorporated into this structure include the metal oxides such as iron and chromium oxides, the precious metal or metal alloy supported materials such as Pt/Al₂O₃, Pt/CeO₂, Pt/CeO₂-ZrO₂, Au/TiO₂ and Au/Fe₂O₃, perovskites including transition metals and other materials having the capability to convert CO to CO₂.

Integration of CO₂ Absorbent

According to one embodiment of the present invention, separate pellets of Rh/Al₂O₃ catalyst and CaO-based CO₂ absorbent are fabricated with a goal of reducing the Rh content to below 0.05 wt.% based on the total mass of absorbent plus reforming catalyst. According to this embodiment, there is substantially no intimate contact between the catalytically active sites (Rh) and the CO₂ absorption sites, the proximity of these species being limited by their relative concentrations, the pellet size and the pellet shape. For example, the pellets can be fabricated with an absorbent to SMR catalyst mass ratio of about 9:1. As a result, the average length scale between the CO₂

generation site and the CO₂ absorption site will be several millimeters (the size of the pellets). There is a strong motivation to further reduce the amount of SMR catalyst (Rh) because it is the most expensive material in this system.

According to another embodiment of the present invention, the powders of the individual Rh/Al₂O₃ catalysts and CaO-based CO₂ absorbents are mixed and pelletized together in the same pellets. The advantage of this approach over using separate pellets is that the mixed powder within each pellet enables a much closer spatial proximity of the SMR catalyst to the absorbent, on the order of 10s to 100s of microns. Also, in contrast to the separate pellet approach, significant changes to the ratio of Rh/Al₂O₃ and CaO-based absorbent can be made with less significant changes in the spatial proximity of the active materials.

In yet another embodiment of the present invention, the Rh/Al₂O₃ and CaO-based absorbent are combined into a single multi-component particle where the active materials are found within the same particle. This is feasible according to the present invention because of compatibility in the spray processing steps (temperature and time history), that can be utilized to make these materials. For example, the Rh reagent can be pre-reacted with the surface of the Al₂O₃ nanoparticles in a solution phase step prior to mixing all the reagents and spray processing. In this embodiment, the spatial proximity between the Rh/Al₂O₃ and CaO-based CO₂ absorbent will be closest, in the range of nanometers to sub-micron and the spatial separation will be least affected by a change in the ratio of the two active materials, such as when they are mixed as separate pellets. This can lead to a significant reduction in the amount of Rh in the integrated absorbent/catalyst pellets and therefore to a reduction in the materials and the overall reactor cost.

Fig. 12 illustrates a type of microstructure according to this embodiment of the present invention. An Al₂O₃ skeleton provides structural support to the absorbent and binds strongly to CaO, based on the formation of well known calcium aluminate compounds such as Ca₅Al₆O₁₄. The distribution of mesoporous CaO throughout this system allows access to the gaseous reagents enabling the CaO to “breathe” CO₂. Comparison of the crystal structures of CaO (NaCl structure, cubic symmetry) and the calcite polymorph of CaCO₃ (trigonal symmetry) shows that they are structurally related,

which explains how CO₂ can be reversibly absorbed by CaO without massive structural breakdown of the material.

The particulate multi-component composite particles can be fabricated utilizing spray processing of precursors to one or more of the materials. Alternatively, the multi-component composite particles can be formed by separately fabricating each of the phases to be included in the particle (e.g., by spray processing), dispersing the materials in a liquid and spray processing the solution to form the dispersion particles.

According to one embodiment, the particulate composite material includes and absorbent phase adapted to absorb CO₂ and a catalyst phase selected from a reforming catalyst phase and a water-gas shift catalyst phase. The mass ratio of the absorbent phase to the catalyst phase is preferably from about 20:1 to about 3:1, more preferably from about 9:1 to about 5:1. The absorbent phase in the composite particles can include an absorbent compound having a reaction fraction of at least about 70 mol.%, and can retain a reaction fraction of at least about 70 mol.% after 100 cycles. Further, the absorbent phase include an absorbent compound that retains at least about 40 mol.% of the theoretical CO₂ absorption capacity of the absorbent compound after at least about 10 cycles, more preferably at least about 60 mol.% and even more preferably at least about 90 mol.% of the theoretical absorption capacity after at least about 10 cycles. The absorbent phase can also retain at least 10 grams of CO₂ per 100 grams of unreacted absorbent after each cycle. Further, the absorbent phase can preferably retain at least about 20 grams CO₂ per 100 grams unreacted absorbent after 10 cycles, more preferably at least about 30 grams CO₂, more preferably at least about 40 grams CO₂ and even more preferably at least about 50 grams CO₂.

Formation of Reactor Bed: Pelletization

Extrusion is the most economic and commonly applied shaping technique for the formation of pellets of catalysts and supports. For extrusion, the catalyst powder is generally in the form of a wet paste or a powder that is converted to a wet paste within the extrusion machine itself. The extrusion machine forces the paste through a die and cuts the extruded material at the desired length. The detailed process can be described as follows.

A slurry of catalyst powder is fed from a hopper into a screw drive. Peptizing agents, such as nitric acid or other organic acids such as acetic acid, may be added to deagglomerate the primary particles by lowering the zeta potential, improving the extrusion process. The screw forces the slurry through holes in the end plate. Usually
5 circular in cross section, these holes can also be made in the shape of cogs or rings, ovals, stars, three-lobed joined rings, or hollow rings similar to macaroni. As the ribbon of slurry emerges from the hole, it begins to dry and harden sufficiently to maintain its shape. The extruder can be equipped with a slicing device, so that the ribbon is either cut into prescribed lengths by the knife rotating outside the end plate or simply allowed
10 to break up as it falls onto a moving belt on its way to the driver.

Extruding equipment can be classed in one of two categories: press extruders and screw extruders. Press extruders are used principally for pastes that are viscous, whereas screw extruders are preferred for thixotropic products. The ease of extrusion and quality of the product depend on the following properties of the paste:

- 15 1. Viscosity (adhesivity): A non-thixotropic product that is too viscous will block the extruder. A product that lacks in viscosity cannot be extruded with a screw and will give extrudates without mechanical resistance when extruded by a press.
- 20 2. Thixotropy (fluidity): Certain substances become less viscous under shearing forces, and then recover their initial state after the forces have been released for a time called the relaxation time. The existence of such thixotropic properties is eminently favorable for the flow of a paste and formation of a solid granule at the exit of a die, providing the relaxation time is short enough.
- 25 3. Stability: Under extrusion conditions, there should be no dynamic sedimentation of the product through exuding water and forming a paste that is too viscous.
- 30 4. Homogeneity: The paste must be homogeneous to assure that the quality of the product is constant. When necessary, the paste is homogenized in a mixer-kneader under controlled conditions of temperature, time, and pH. An excess of kneading can in fact compact

the material and suppress potential macropores. Screw extruders partially knead the paste as it travels along the screw.

Even for a given charge with specific properties, the operating variables are rather poorly defined and are closely related to the type of equipment. Generally they include: mixing time, water content, adhesives content, paste aging and extrusion temperature. In the case that a powder does not have certain level of fluidity or plasticity, various additives can be used to aid the pre-forming of pastes or microgranules, such as:

1. Lubricants for improving the rheological behavior, such as liquid (water, mineral oil) or solid (starch or clays like montmorillonite, stearic acid, and various stearates);
2. Binders (aluminas or clays). Binders are added to also increase the post-compression adhesion, as for example starch is added for palletizing/extrusion of active carbon;
3. Peptizing agents such as dilute acetic or nitric acid to deagglomerate the particles. By peptizing, an increase in the adhesive forces due to chemical bonds resulting from contact between the pastes can be achieved, meanwhile the particle surfaces are made more chemically reactive; and
4. Combustible materials to increase the porosity (the so-called pore-formers like carbon black, graphite, talc, starch, etc.).

If the extrusion is performed well, the particles (extrudates or pellets) formed are very regular, hard, and uniform. However, if the extrusion is uneven and the rate of extrusion from one section of the dies is different from that of another section, the particle length can be quite variable and the hardness and sharpness of the ends can also be variable. The extruder, however, can rapidly produce great quantities of product of various shapes and as a consequence is relatively inexpensive in comparison with pilling or pelletizing.

In practice, the particulate catalysts and absorbents have to be pelletized to meet a certain crush strength. Pelletization of powders typically involves reaction of the powders to be pelletized with a binder and extrusion of the paste through a die to give

the desired pellet geometries. In the case of catalysts and gas absorbent materials, the binder system is typically Al_2O_3 combined with a peptizing agent such as an organic acid. On reaction, these materials yield a metal-organic compound that penetrates the entire structure and on subsequent thermal decomposition yields a continuous Al_2O_3 skeleton that provides mechanical support. Ideally, the extrudates will maintain the high reactivity and high cycle ability of the original powder after pelletizing.

There are a number of approaches to pelletization. One is directly pelletizing the original powders (e.g., CaO) that show high reactivity to CO_2 carbonation. Another is pelletizing an intermediate powder precursor like CaC_2O_4 and CaCO_3 with a certain amount of binder. After post-processing, the decomposition of precursors into CaO will facilitate the formation of the microstructure and porosity of the extrudates, and the obtained pellets will maintain or even improve the absorbent performance during carbonation/decarbonation cycles. In this approach, however, the amount of binder used for extrusion should be carefully considered to achieve maximum capacity for CO_2 removal.

According to one embodiment, a pellet includes at least about 5 wt.% of a particulate intermediate compound to an absorbent compound where the particulate intermediate compound has a theoretical density that is not greater than the theoretical density of the absorbent compound and wherein the particulates are substantially spherical. The pellet can preferably have a crush strength of at least about 1 N/mn. The pellet can include, for example, alumina as a binder.

Formation of Reactor Bed: Coated Structures

The pelletization of the materials described above is only one of a number of methods to create a reactor bed for AER. The advantages of a pelletized bed are that the capacity of the bed is relatively high. However, under some circumstances, the operating space velocity of such a pelletized reactor bed can limit the performance of the overall system. Therefore, as according to another embodiment of the present invention, the materials can be coated onto a surface that provides a high available surface area for the powder. The structures that are typically coated are high surface area structures such as porous monoliths, honeycomb structure monoliths or corrugated

support structures. These support structures are typically comprised of metals or metal oxides to aid in thermal stability and in some cases to improve thermal conductivity.

In order to coat the support structures, the powders are often formed into a slurry, paste or ink that is then applied to the support surface. Methods to coat the powders described herein onto the surface of the support structures may include wash-coating, dipping, screen printing, ink-jet printing, spraying or any other printing or coating, digital or analog technologies known to those skilled in the art.

Formation of Reactor Bed: Textile, Cloth or Paper Support

While the advantage of the coated structures is that the space velocity of the system can be increased, one potential limitation of the coated structures is a reduction in capacity. In order to achieve a better compromise between the capacity and space velocity characteristics of coated structures and pellets, the materials described herein can be incorporated into porous cloths. The cloths may be comprised of woven or non-woven fibers of a variety of different materials including various metals (for example, copper, nickel or stainless steel), metal oxides or carbon fibers. In a preferred embodiment, the powders are incorporated into a metal-based cloth to improve the thermal characteristics of the powder bed.

In order to coat the cloth structures, the powders are often formed into a slurry, paste or ink that is then applied to the cloth surface. Methods to coat the powders onto the surface of the cloth structures may include wash-coating, dipping, screen printing, ink-jet printing, spraying or any other printing or coating, digital or analog technologies known to those skilled in the art.

In another embodiment, the powders may be incorporated into the bulk of the textile, cloth or paper at the time of the manufacture of the textile, cloth or paper support. In the typical paper or non-woven cloth manufacturing process, the powders are mixed with the fibers in the original slurry and as the suspended materials are removed from the slurry, the powders are trapped inside the structure of the material. Post processing may be necessary to achieve some chemical attachment between the particles and the support to complement the mechanical entrapment within the pore structure created by the fibers.

AER

In accordance with the foregoing description and the following examples, the materials of the present invention can advantageously been utilized in an absorption enhanced reforming (AER) process for the conversion of a carbon-based fuel to a hydrogen-rich product gas. The carbon-based fuel is preferably a hydrocarbon-based fuel, such as a gaseous hydrocarbon fuel or a liquid hydrocarbon fuel. Preferred gaseous fuels are those that include methane (e.g., natural gas) and preferred liquid fuels include diesel fuel, JP-8 aviation fuel, kerosene, ethanol and gasoline.

According to one embodiment, the carbon-based fuel is contacted with at least a first conversion catalyst such as an SMR catalyst and optionally a WGS catalyst to catalyze the formation of an intermediate gas product that includes H_2 from the carbon-based fuel. Other components can be provided with the carbon-based fuel, such as steam (e.g., Equation 1), oxygen (e.g., air as in Equation 5) or a mixture of oxygen and steam. The intermediate gas product includes CO_2 and is contacted with an absorbent to absorb CO_2 and form a H_2 rich gas. It is preferred that the carbon-based fuel contact the catalyst and the absorbent at a temperature of not greater than about $800^{\circ}C$. The H_2 -rich gas is extracted from the contacting step and preferably has a H_2 content of at least about 95 mol.%, more preferably at least about 98 mol.%.

Thereafter, the absorbent is regenerated by decarbonizing the absorbent to complete the cycle. Regeneration of the absorbent can include heating the absorbent to an elevated temperature, such as at least about $700^{\circ}C$, possibly in the presence of water or another reagent.

According to the present invention, the absorbent can be cycled (i.e., absorbing CO_2 and then regenerating to remove substantially all of the chemically bound CO_2) at least ten times, wherein the absorbent retains at least about 50 mol.% of its theoretical absorption capacity based on the quantity of active absorbent compound present for every cycle through ten cycles. According to certain preferred embodiments of this aspect of the present invention, the absorbent can retain at least about 50 mol.% of its theoretical absorption capacity for every cycle up to 50 cycles, more preferably up to 100 cycles and even more preferably up to 500 cycles. Further, the absorbent can preferably retain at least about 70 mol.% of its theoretical absorption capacity for every

cycle up to ten cycles and more preferably that the absorbent retains at least about 90 mol.% of its theoretical absorption capacity for every cycle up to ten cycles. In one embodiment, the absorbent is cycled at least 200 times and the absorbent retains at least about 10% of its theoretical absorption capacity, more preferably at least about 25% of its theoretical absorption capacity and even more preferably at least about 50% of its theoretical absorption capacity after 200 cycles.

The absorbent materials according to the present invention also have a high initial absorption capacity for CO₂. According to one embodiment, the initial absorption capacity (expressed as a reaction fraction of active absorbent compound) is at least about 60 mol.%, and more preferably is at least about 70 mol.%. As is discussed above, the absorbent and/or the catalyst can be pelletized or can be coated onto a rigid or semi-rigid support structure.

According to another embodiment, the total mass of the absorbent material retains at least about 10 grams of CO₂ per 100 grams unreacted absorbent after each of the cycles. More preferably, the absorbent material retains at least 20 grams CO₂ per 100 grams unreacted absorbent after each of the cycles, even more preferably at least about 30 grams CO₂ per 100 grams unreacted absorbent after each of the cycles, even more preferably at least about 40 grams CO₂ per 100 grams unreacted absorbent after each of the cycles and even more preferably at least 50 grams CO₂ per 100 grams unreacted absorbent after each of the cycles. Further, such high absorption capacity can be achieved over 50 cycles, over 100 cycles and even over 500 cycles.

According to another embodiment, the absorbent material can be cycled at least 50 times wherein the absorbent material retains at least about 20 mol.% of its theoretical CO₂ absorption capacity after each cycle. More preferably, the absorbent material retains at least about 40 mol.% of its theoretical CO₂ absorption capacity, even more preferably at least about 60 mol.% and even more preferably at least about 90 mol.%. The absorbent material can preferably retain at least about 20 grams CO₂ per 100 grams unreacted absorbent material after each cycle, even more preferably at least about 30 grams CO₂ per 100 grams unreacted absorbent material after each cycle, even more preferably at least about 40 grams CO₂ per 100 grams unreacted absorbent material after each cycle, and even more preferably at least about 50 grams CO₂ per

100 grams of unreacted absorbent material after each cycle. Further, the absorbent material can be cycled at least 100 times when the absorbent material retains at least about 20 mol.% of its theoretical CO₂ absorption capacity.

According to one embodiment, the absorbent material includes an absorbent
5 compound and an inert compound such as a metal oxide. The absorbent material preferably has an absorption capacity of at least about 10 grams CO₂ per 100 grams of absorbent material after 100 cycles, more preferably at least about 20 grams CO₂ and even more preferably at least about 30 grams CO₂. The absorbent compound contained within the absorbent material preferably has an absorption capacity of at least
10 about 50 mol.% after 100 cycles, more preferably at least about 70 mol.% and even more preferably at least about 90 mol.%.

It is also an advantage of the present invention that the absorbent does not undergo large fluctuations in bulk density over numerous cycles. The bulk density of the materials described in the present specification is defined as the mass of the
15 particles divided by the volume they occupy, including the pore spaces between the particles. This volume includes the solid material volume, the open and closed pore volume within the particles, as well as the interparticle void volume. The bulk density of the material is typically derived from a mercury porosimetry measurement. Specifically, according to one embodiment, the absorbent is formed into a pellet having a first bulk
20 density. The pellet can then be used in an AER reaction, substantially as described above, and the pelletized absorbent will carbonize upon absorption of CO₂ to form a carbonized pellet having a second bulk density. After the pellet is regenerated back to the absorbent material, it will have a third bulk density. Using commercially available absorbent materials, the second bulk density is much lower than the first bulk density
25 and the third bulk density would be similar to the first bulk density. According to the present invention, however, the second bulk density is not significantly different than the first bulk density and the third bulk density is much higher than the first bulk density. The third bulk density is preferably greater than 100% of the first bulk density, such as up to about 140% of the first bulk density.

30 The SMR catalysts such as Rh/Al₂O₃ fabricated according to the present invention also have improved performance as compared to the prior art. Specifically,

the SMR catalyst can have a high conversion efficiency for the conversion of a carbon-based fuel to hydrogen. According to one embodiment, the SMR catalyst achieves at least about 90% of the theoretical thermodynamic conversion of methane to hydrogen at a temperature of 600°C, a H₂O:C molar ratio of 3:1 and a gas hour space velocity (GHSV) of 5000 hour⁻¹ in the absence of an absorbent for CO₂. Preferably, the catalyst can achieve at least about 95% of the theoretical thermodynamic conversion under the same conditions. Further, the reforming catalyst can preferably achieve at least about 90% of the theoretical thermodynamic conversion of methane to hydrogen at a temperature of 600°C, a molar H₂O:C ratio of 3:1 and a gas hour space velocity of 10,000 hour⁻¹ in the absence of an absorbent for CO₂. Preferably, the reforming catalyst can also obtain at least about 90% of the theoretical thermodynamic conversion under the same conditions but at a gas hour space velocity of 12,500 hour⁻¹.

Integration of AER with a Fuel Cell Stack

One of the applications of the single-step reformer (SSR) is as a cost-effective hydrogen source for stationary residential fuel cells that run on natural gas. The benefits of SSR, particularly the purity of the hydrogen stream, combined with the potential benefits of using existing metal hydride storage materials, leads to a strong impact on the capital cost and operating efficiency of the fuel cell stack, especially in stationary fuel cell applications including in back-up power units for uninterruptible/emergency power supply applications, as well as residential and commercial applications.

The significance of the SSR reformer on the fuel cell stack capital cost and efficiency is as follows. A state of the art natural gas reformer based on the competing technologies of steam methane reforming and autothermal reforming produces a gas feed for the fuel cell anode that is in the range of 40% - 50% H₂ with the balance being nitrogen, CO₂, water and CO at ppm levels. This gas composition, containing a relatively dilute H₂ feed, results in a relatively low power density in the fuel cell stack, the requirement for a relatively high loading on PtRu alloy (to provide CO tolerance) on the anode and reliability problems that are believed to be associated with the reverse water-gas shift reaction where the PtRu alloy converts the CO₂ and H₂ present to water

and CO (thus poisoning the electrocatalyst). In contrast, the gas feed from the SSR system, which due to its high H₂ content and low impurity content, can uniquely be coupled directly with the existing metal hydride hydrogen storage materials has an enormous impact on the cost and operation of the stack. The purer hydrogen feed at a much higher concentration may avoid the need for PtRu alloy on the anode altogether and could lead to a significantly increased power density in the stack resulting in a significant reduction in the size (i.e., number and/or size of MEAs) required to achieve a particular power output. Start-up issues are avoided because the hydrogen storage materials are built into the hydrogen purification system. Furthermore, the H₂/air fuel cell stack technology (which can now be used due to the performance of the SSR reformer) is much more mature and reliable compared to the reformed natural gas/air fuel cell technology that is required when the SMR and ATR technology is used. Since it is calculated that around 40% of the fuel cell stack cost is based on the cost of the MEAs, this impact could clearly be significant in reduction of capital and operating cost.

Examples

The following examples illustrate the production and application of the AER materials according to the present invention, including absorbents, SMR catalysts and multi-functional composite materials.

Absorbents

The absorbent materials according to the present invention can be fabricated by spray pyrolysis or spray drying, and either fabrication method can be followed by post-processing. The following specific examples illustrate some of these embodiments.

Example A-1

This example illustrates the production of a 5g batch of Ca-oxide (CaO) absorbent according to the present invention by spray pyrolysis. 21g of Ca-nitrate (Ca(NO₃)₂) is dissolved in 178g of de-ionized water. 1g of lactic acid and 1g of NH₄-nitrate (NH₄NO₃) is added while stirring and the solution is stirred for 10 minutes. Spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 900°C, with air as both the carrier gas and the quench gas at 60 SLPM and 5 SCFM,

respectively. The reaction residence time of the system is 1.5 seconds, as calculated by the quotient of the system volume and the carrier gas flow rate corrected for temperature expansion. The collected powder batch consists essentially of CaO.

5 Example A-2

This example illustrates the fabrication of a 1kg batch of Ca-oxalate (CaC_2O_4) according to the present invention using a spray dryer. 1.84kg of Ca-nitrate is dissolved in 2kg of de-ionized water and 1.11kg of NH_4 -oxalate is dissolved in 4.5kg of de-ionized water. The two solutions are individually mixed on shear mixers for 30 minutes. The Ca-nitrate solution is slowly added to the NH_4 -oxalate solution while shearing. The resulting 10 wt.% solids dispersion of precipitated Ca-oxalate is sheared for an additional hour. The precursor dispersion is fed into a mixed-flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F (524°C/304°C), using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system is 10 seconds as calculated by the quotient of the system volume and the gas flow rate corrected for expansion using the outlet temperature. The powder is collected using a cyclone. The powder batch consists essentially of CaC_2O_4 .

Example A-3

20 This example illustrates the fabrication of a 1kg batch of CaC_2O_4 and 5% Al_2O_3 according to the present invention in a spray dryer. 1.74kg of Ca-nitrate is dissolved in 2kg of de-ionized water and 1.06kg of NH_4 -oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) is dissolved in 5kg of de-ionized water. The two solutions are individually mixed on shear mixers for 30 minutes. The Ca-nitrate solution is slowly added to the NH_4 -oxalate solution while shearing to precipitate CaC_2O_4 . The resulting 10 wt.% solids dispersion of precipitated CaC_2O_4 is sheared for an additional hour. 0.25kg of DISPAL 23N4-20 (a 20% boehmite alumina dispersion in water, available from Sasol, North America) is added, followed by 15 minutes of shear mixing. The precursor dispersion is fed into a mixed-flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system is 10

seconds, as calculated above. The powder is collected using a cyclone. The powder batch consists essentially of 5 wt.% Al_2O_3 and 95 wt.% CaC_2O_4 .

Example A-3A

5 CaC_2O_4 , 25% Al_2O_3 ; 1kg batch

This example illustrates the fabrication of a powder batch consisting essentially of CaC_2O_4 with 25% Al_2O_3 . 1.38kg of Ca-nitrate is dissolved in 2kg of de-ionized water. 0.84kg of NH_4 -oxalate is dissolved in 5kg of de-ionized water. The two solutions are mixed on shear mixers individually for 30 minutes. The Ca-nitrate solution is slowly added to the NH_4 -oxalate solution while shearing. The resulting 10 wt.% solids dispersion of precipitated Ca-oxalate is sheared for an additional hour. 1.25kg of DISPAL 23N4-20 is added, followed by 15 minutes of shear mixing. The precursor dispersion is fed into a mixed flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system is 10 seconds, as defined above. The powder is collected using a cyclone and consists essentially of CaC_2O_4 and Al_2O_3 .

Example A-4

This example illustrates the fabrication of a $\text{CaCO}_3/\text{Al}_2\text{O}_3$ composite by spray drying and post-processing according to the present invention. 140g of a powder consisting essentially of CaC_2O_4 and 5% Al_2O_3 (Example A-3) is put into 2 quartz boats, which are then loaded into a tube furnace. Under flowing air, the furnace is ramped 10°C/min to 500°C, held for 3 hours and is then cooled to room temperature. The resulting powder consists essentially of CaCO_3 and Al_2O_3 .

Example A-5

This example illustrates the fabrication of a powder batch consisting essentially of CaCO_3 and CaO with Al_2O_3 by spray drying and post-processing according to the present invention. 140g of a powder consisting essentially of CaC_2O_4 and 5% Al_2O_3 made by spray drying (Example A-3) is put into 2 quartz boats, which are then loaded into a tube furnace. Under flowing air, the furnace is ramped 10°C/min to 750°C, held

for 3 hrs and is then cooled to room temperature. The resulting powder consists essentially of a mixture of CaCO_3 , CaO and Al_2O_3 .

Example A-6

5 This example illustrates the fabrication of a 500g batch of a powder consisting essentially of $\text{CaC}_2\text{O}_4:\text{MgC}_2\text{O}_4$ with a calculated $\text{CaO}:\text{MgO}$ wt. ratio of 50:50 according to the present invention. Individually, 0.92kg of Ca-nitrate is dissolved in 1.0kg of de-ionized water, 0.54kg of NH_4 -oxalate is dissolved in 2.5kg of de-ionized water, 1.0kg of Mg-nitrate ($\text{Mg}(\text{NO}_3)_2$) is dissolved in 1.0kg of de-ionized water, and 0.56kg of NH_4 -oxalate is dissolved in 1.8kg of de-ionized water. These solutions are shear mixed for 10 30 minutes. Separately, the nitrate solutions are added to the oxalate solutions. The two resulting dispersions of Ca-oxalate and Mg-oxalate are sheared separately for 1 hour and are then combined. The resulting 10 wt.% solids dispersion of precipitated Ca-oxalates and Mg-oxalates is sheared for an additional hour. The precursor 15 dispersion is fed into a mixed-flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of $975^\circ\text{F}/580^\circ\text{F}$, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system used is 10 seconds, as defined above. The powder is collected using a cyclone and consists essentially of $\text{CaC}_2\text{O}_4:\text{MgC}_2\text{O}_4$.

20 Example A-7

This example illustrates the fabrication of a powder batch consisting of a mixture of CaCO_3 and $\text{CaO}:\text{MgO}$ by spray drying and post-processing according to the present invention. 320g of a $\text{CaC}_2\text{O}_4:\text{MgC}_2\text{O}_4$ powder made on a spray dryer and with a calculated $\text{CaO}:\text{MgO}$ wt. ratio of 50:50 (Example A-6) is put into shallow pans, which 25 are then loaded into a convection oven. Under flowing air, the furnace is ramped $10^\circ\text{C}/\text{min}$ to 500°C , held for 3 hours, and is then cooled to room temperature. The resulting powder batch consists essentially of CaCO_3 and $\text{CaO}:\text{MgO}$.

Example A-8

30 This example illustrates the fabrication of a powder batch consisting essentially of 95 wt.% CaCO_3 and CaO with 5 wt.% Al_2O_3 by spray drying and post-processing

according to the present invention. A powder batch consisting essentially of CaC_2O_4 and 5% Al_2O_3 , (which is made the same method as Example A-3), is put into a screw feeder and delivered to a rotary calciner comprising an elongated tube at a rate of 1 kg/hr. The tube includes three equal-length heating zones that are set to 450°C, 750°C and 750°C respectively. Air is delivered in a counter-current configuration at a rate of 112 SCFH. The elongated tube is set with an angle and rotational rate in order to yield a residence time of 24 minutes.

Example A-9

This example illustrates the fabrication of a 3kg powder batch consisting essentially of $\text{CaC}_2\text{O}_4\text{:MgC}_2\text{O}_4$ (with a calculated CaO:MgO wt. ratio of 80:20). Individually, 4.24kg of Ca-nitrate is dissolved in 5kg of de-ionized water, 4.11kg of NH_4 -oxalate is dissolved in 6kg of de-ionized water, 1.6kg of Mg-nitrate is dissolved in 2kg of de-ionized water and 1.43kg of NH_4 -oxalate is dissolved in 5kg of de-ionized water. These solutions are shear mixed for 30 minutes. Separately, the nitrate solutions are added to the oxalate solutions. The two resulting dispersions of Ca-oxalate and Mg-oxalate are sheared separately for 1 hour then combined. The resulting 10 wt.% solids dispersion of precipitated Ca-oxalate and Mg-oxalate is sheared for an additional hour. The precursor dispersion is fed into a mixed-flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system used is 10 seconds, as calculated above. The powder is collected using a cyclone and consists essentially of $\text{CaC}_2\text{O}_4\text{:MgC}_2\text{O}_4$.

Example A-10

This example illustrates the fabrication of a powder batch consisting essentially of a mixture of CaCO_3 and CaO:MgO by spray drying and post-processing according to the present invention. 200g of a powder consisting essentially of $\text{CaC}_2\text{O}_4\text{:MgC}_2\text{O}_4$ (calculated CaO:MgO wt. ratio of 80:20, Example A-9) is put into shallow pans, which are then loaded into a convection oven. Under flowing air, the furnace is ramped

10°C/min to 500°C, held for 3 hrs and is then cooled to room temperature. The resulting powder batch consists of a mixture of CaCO₃ and CaO:MgO.

Example A-11

5 This example illustrates the fabrication of a mixture of CaCO₃ and CaO:MgO by spray drying and post-processing according to the present invention. 200g of CaC₂O₄:MgC₂O₄ (80:20 ratio, Example A-9) is put into shallow pans, which are then loaded into a convection oven. Under flowing air, the furnace is ramped 10°C/min to 750°C, held for 3 hrs and is then cooled to room temperature.

10 The foregoing examples illustrate several different fabrication methods for absorbent materials according to the present invention. A number of additional examples including CaO and/or CaCO₃ are prepared in a similar fashion and these additional examples are summarized in Table 4. Table 4 lists absorbent materials that are obtained by different methods including spray pyrolysis (SP) and spray drying (SD)

15 with post-processing (PP). Commercial grade CaO (available from J.T. Baker, Phillipsburg, NJ, USA) is also listed for comparison.

Table 4

Example	Composition	Precursor	Method
A-12	CaO, CaCO ₃	Example A-2	PP at 500°C for 3 hrs
A-13	CaO, CaCO ₃	Example A-2	PP at 750°C for 3 hrs
A-14	CaO	Ca-nitrate NH ₄ -nitrate Lactic acid	Spray pyrolysis at 900°C
A-15	CaO	Ca-nitrate NH ₄ -nitrate	Spray pyrolysis at 900°C
A-16	CaO	Ca-nitrate 20% NH ₄ -nitrate 2.5% PVP (10k)	Spray pyrolysis at 1000°C
CaO1	CaO	Commercial Grade	N/A

Table 5 summarizes a number of additional absorbent examples that include

20 CaO with MgO and/or Al₂O₃ that are prepared by various methods according to the present invention.

Table 5

Example	Composition (nominal, expressed as oxides)	Precursor	Method
A-17	CaO:MgO (50:50 by wt.) 5% Al ₂ O ₃	Ca-nitrate/NH ₄ -oxalate Mg-nitrate/NH ₄ -oxalate DISPAL 23N4-20	Spray dryer
A-18	CaO:MgO (50:50 by wt.) 5% Al ₂ O ₃	Example A-17	Post-processing at 500°C for 3 hrs
A-19	CaO:MgO (90:10 by wt.)	Ca-nitrate/NH ₄ -oxalate Mg-nitrate/NH ₄ -oxalate	Spray dryer
A-20	CaO:MgO (90:10 by wt.)	Example A-19	Post-processing at 500°C for 3 hrs
A-21	CaO:MgO (90:10 by wt.) 5% Al ₂ O ₃	Ca-nitrate/NH ₄ -oxalate Mg-nitrate/NH ₄ -oxalate DISPAL 23N4-20	Spray dryer
A-22	CaO:MgO (90:10 by wt.) 5% Al ₂ O ₃	Example A-21	Post-processing at 500°C for 3 hrs
A-23	CaO:MgO (50:50 by at.%)	Ca-nitrate/Mg-nitrate glycine lactic acid	Spray pyrolysis
A-24	CaO:MgO (50:50 by at.%)	Ca-nitrate/Mg-nitrate urea ethanol	Spray pyrolysis
A-25	CaO:MgO (50:50 by at.%)	Ca-nitrate/Mg-nitrate glycine ethanol	Spray pyrolysis
A-26	CaO:MgO (50:50 by at.%)	Ca-nitrate/Mg-nitrate	Spray pyrolysis
A-27	CaO 43 wt.% Al ₂ O ₃	Ca-nitrate NH ₄ -oxalate Al ₂ O ₃	Spray Dryer
A-28	CaO 43 wt.% Al ₂ O ₃	Example A-27	Post-process at 500°C for 3 hrs

The additives to the precursor compositions in Examples A-23, A-24 and A-25 (namely glycine, lactic acid, urea and ethanol) are porosity-enhancing agents for the purpose of introducing additional porosity into the absorbent materials.

Table 6 lists the particle size distribution (PSD), BET surface area, average pore diameter and pore volume for select absorbent examples. For the examples in Table 6 and the following examples herein, the PSD is measured by laser light scattering, such as in a MICROTRAC instrument (Microtrac, Inc., Montgomeryville, PA). The BET surface area is measured by nitrogen adsorption and the average pore diameter is

measured by BJH adsorption. The pore volume is measured by nitrogen adsorption and is the pore volume only for pores having a diameter of not greater than about 100 nanometers.

Table 6

Example	PSD d10, d50, d90 (μm)	BET Surface Area (m^2/g)	Average Pore Diameter (nm)	Pore Volume (cm^3/g)
A-2	2.0, 5.0, 13.0	19.6	10.6	0.0517
A-3	2.3, 5.7, 16.0	24.5	16.5	0.101
A-4	1.7, 4.4, 11.7	17.7	13.1	0.058
A-5	3.7, 10.3, 25.0	18.9	12.5	0.059
A-6	1.3, 3.0, 6.0	24.2	13.9	0.084
A-7	3.1, 6.7, 14.3	60.1	16.1	0.242
A-8	5.5, 14.8, 26.8	N/A	N/A	N/A
A-10	N/A	27.8	13.4	0.093

Fig. 13 compares the particle size distribution (d_{10} , d_{50} and d_{90}) of commercial grade CaO, CaO prepared by spray pyrolysis and CaO/ Al_2O_3 powders prepared by spray conversion of oxalate precursors in a spray dryer and post-processing of the intermediate compound. While the d_{50} of the commercial CaO powder is approximately 30 μm , the d_{50} of CaO powder made by spray pyrolysis (Example A-16) is less than 10 μm and for the Ca-oxalate intermediate compound (Example A-2) is less than 5 μm . Post-processing of Ca-oxalate at 750°C to convert it to CaO (Example A-13) increases the d_{50} from 5 μm to about 20 μm , while the addition of Al_2O_3 as an additive and post-processing at 750°C (Example A-5) reduces the sintering and d_{50} increases to only about 10 μm . The addition of other inert additives such as MgO has a similar effect and prevents an increase of the absorbent particle size distribution after repetitive cycles.

Fig. 14 compares the BET surface area of the examples illustrated in Fig. 13. While the BET surface area of the commercial CaO powder is less than 2 m^2/g , the surface area of the absorbent materials prepared by spray processing according to the present invention is significantly higher.

Fig. 15 compares the measured pore volume (pores < 100 nanometers) of the examples illustrated in Figs. 13 and 14. The pore volume is less than 0.01 cm^3/g for the conventional CaO powder and at least two times higher for the absorbent powders

prepared by spray processing methods. The addition of inert additive such as alumina (Example A-3) leads to an even higher increase of the pore volume (e.g., up to 0.06 cm³/g).

Cycling of Absorbents

5 Fig. 16 illustrates the carbonation and decarbonation kinetics of CO₂ by commercially available CaO (J.T. Baker) measured by thermogravimetric analysis (TGA). Fig. 16 illustrates that the carbonation of CaO is divided into two distinct regions, the fast region and the slow region. The fast region (less than 800 seconds) corresponds to the easy access to CaO active sites present on the external surface and
10 the slow region (1000 to 10,000 seconds) corresponds to the penetration of CO₂ through the carbonate layer into unreacted CaO near the particle core. The portion of CaO reactivity and kinetics in these two regions depend on the material properties and operating conditions. Decarbonation takes place (>10,000 seconds) when the bed temperature is raised up to 750°C or higher. Fig. 16 illustrates that the overall
15 absorption capacity, expressed as a CaO reaction fraction is around 40 mol.% at a time of 10000 seconds. As used herein, the CaO reaction fraction is the ratio of CaO converted to CaCO₃ relative to the amount of available absorbent compound (e.g., CaO) in the absorbent material, usually expressed as a mol.%.

 Based on this interpretation, for the standard sample measurements illustrated in
20 Fig. 16, about 50% of the total absorption capacity is consumed by the available surface area of the absorbent, and the remaining 50% of the capacity requires a long reaction time. It is therefore advantageous to increase the absorbent available surface area to enable faster absorption. This is illustrated in more detail below.

 Fig. 17 illustrates the absorption performance of the commercial CaO sample
25 over 26 cycles with the carbonation at 600°C and decarbonation at 750°C. For these examples a cycle of absorbent-containing material includes heating the sample disposed in a crucible in a thermo-gravimetric analysis (TGA) unit to 750°C or 800°C at a rate of 10-20°C/min in the presence of N₂ until the TGA baseline is stable. The crucibles are then cooled down to the carbonation temperature (600°C), and pure CO₂
30 is introduced into the chamber. Once the stable baseline is reached, decarbonation

starts by switching the gas to N₂ and raising the temperature to 750°C or 800°C. The weight loss of the absorbent is then recorded as a function of time until a stable weight is reached and the sample is then cooled down to room temperature. All carbonation takes place at 600°C, and the sample pre-treatment and decarbonation temperature are

5 kept the same.

Referring to Fig. 17, the initial absorption capacity of the commercial CaO is about 22g CO₂/100g of sample and the peak absorption capacity is about 35g CO₂/100g of sample. It is noteworthy that the absorption capacity fluctuates from about 15g to 35g CO₂/100g of sample. Such fluctuations in absorption capacity are
10 undesirable for commercial operations since the device must then be designed to accommodate the lowest capacity (e.g., to accommodate 15g CO₂/100g of sample).

Figs. 18 and 19 illustrate the change in particle size distribution (d₁₀, d₅₀ and d₉₀), pore volume (pores <100 nanometers), BET surface area and pore diameter for the commercial CaO powder after 27 cycles. It is evident that sintering of the powder has
15 occurred, resulting in a significant increase in average particle size (Fig. 18). The pore volume and average pore diameter decreased slightly and the BET surface area increased slightly (Fig. 19).

Table 7 summarizes the change in BET surface area, pore volume and pore diameter after cycling select absorbent materials according to the present invention 12
20 times.

Table 7

Example	As-Made			After 12 Cycles		
	BET (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	BET (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
A-7	60.1	0.242	16.1	12.37	0.0612	19.5
A-18	61.7	0.235	15.2	7.97	0.044	22.2
A-22	17.5	0.055	14	6.07	0.019	12.7
A-20	15.7	0.066	15.1	2.7	0.012	17.5
A-4	17.7	0.019	9.7	5.48	0.012	8.9
A-12	7.7	0.058	13.1	0.66	0.001	8.5
A-16	5.6	0.057	13.2	1.65	0.033	8.11

Fig. 20 illustrates the absorption capacity in terms of CaO reaction fraction through multiple cycles for commercial CaO (3 samples) and CaO obtained from different spray processing methods, namely spray pyrolysis (Examples A-14 and A-15), and conversion in a spray dryer with post-processing (Examples A-12 and A-13).

Referring to Fig. 20, the capacity of some CaO absorbents made by spray pyrolysis is only slightly higher compared to the commercial CaO absorbents (30 mol. % vs. 25 mol.% CaO reaction fraction in the first cycle). It can also be seen that CaO samples from oxalate precursors (Example A-12, by XRD CaCO_3 and Example A-13, by XRD a mix of CaCO_3 and CaO, made by spray drying followed by post-processing at 500°C and 750°C, respectively) have a high initial absorption capacity - up to 80 mol.% CaO reaction fraction, nearly three times higher than commercial CaO. These results clearly demonstrate the advantages of spray processing in the development of CaO-based absorbents. However, the absorption capacity decreases very rapidly after a limited number of cycles (from 85 mol.% to 32 mol.%) due to the loss of microstructure and porosity, as mentioned above. Therefore, further addition of materials into CaO is necessary to prevent the materials from sintering during temperature swing operation and to maintain the cyclability.

Fig. 21 illustrates a comparison between the initial carbonation and decarbonation profiles of CaO absorbent materials from different sources including a commercial samples. The CaO fabricated from calcium nitrate and ammonium oxalate precursors and post processed at 500°C (A-12) or at 750°C (A-13) has faster kinetics and higher reactivity in the fast region and improved kinetics upon decarbonation.

Figs. 22 and 23 illustrate the particle size distribution (Fig. 22) and the pore volume, average pore diameter (pores < 100 nanometers) and BET surface area (Fig. 23) for Examples A-4, A-12, A-5 and A-13. It is evident that the addition of 10% Al_2O_3 reduces the initial particle size of the absorbent materials (Example A-4 compared to Example A-12 and Example A-5 compared to Example A-13) and increases the average pore volume and surface area of the powders.

Fig. 24 illustrates the CaO absorption capacity in terms of CaO reaction fraction as a function of the number of cycles for 3 different examples. The addition of 10 wt.%

Al₂O₃ to CaO in Examples A-4 and A-5 can significantly improve the absorbent stability while maintaining the original high CO₂ absorption, retaining an absorption capacity above 70 mol.% for each cycle up to 12 cycles. One reason for good cyclability of 10 wt.% Al₂O₃/CaO samples is the particle size stability after the multiple cycles, as demonstrated in Table 8.

Table 8

Example	Composition	Particle Size (μm) d ₁₀ , d ₅₀ , d ₉₀	
		Before Cycling	After Cycling
A-12	100% CaO	2.0, 5.1, 13.2	5.6, 14.5, 26.2
A-4	90% CaO 10% Al ₂ O ₃	1.7, 4.4, 11.7	1.0, 2.7, 11.4
A-28	57% CaO 43% Al ₂ O ₃	1.2, 5.9, 17.1	3.2, 7.5, 22.4

It is noteworthy that the PSD for Example A-4 actually decreases after cycling.

Figs. 25(a) and (b) illustrate the SEM photomicrographs of a commercially available CaO powder before and after 27 cycles. Figs. 26(a) and (b) illustrate SEM photomicrographs of Example A-12 before and after 12 cycles. Figs. 27(a) and (b) illustrate SEM photomicrographs of Example A-4 before and after 12 cycles.

Fig. 28 illustrates the change in particle size distribution for Al₂O₃/CaO examples according to the present invention before and after 12 cycles. It is evident that the examples having good recyclability (Examples A-4 and A-5) also exhibit an overall decrease in particle size. Example A-28 (43% Al₂O₃) shows an increase in the d₅₀ and d₉₀ size ranges.

MgO can also be added to the absorbent materials in accordance with the present invention. Fig. 29 illustrates the performance achieved by adding MgO into CaO at different ratios of CaO:MgO and also by adding Al₂O₃. It can be seen that CaO:MgO with different ratios (from 90:10 to 50:50) made by spray drying followed by post processing at 500°C have a similar initial absorption capacity in terms of CaO reaction fraction. However, the stability is quite different – only a CaO:MgO ratio of 50:50 stabilizes the recyclability. Example A-7 with a CaO:MgO ratio of 50:50 retains a capacity of over 90% even after 12 cycles, while the capacity of Example A-20 with a CaO:MgO ratio of 90:10 decreases to less than 60% after 12 cycles. The initial

differences of carbonation/decarbonation kinetics among samples with the same composition depend on the specific conditions used for spray processing, as is illustrated in Fig. 30. However, both Example A-26 made by spray pyrolysis and Example A-7 made by spray drying followed by post-processing at 500°C have similar carbonation/decarbonation rates. This observation supports the conclusion that absorbents with good absorption kinetics and recyclability can be derived by various spray processing methods, as described in detail above, as long as the right combination of composition and processing conditions have been utilized.

As shown above, absorbents with various compositions deliver high reactivity for CO₂ absorption in terms of mol.% fraction of CaO. The composition of the inert additives is not limited to Al₂O₃ and MgO - other oxides such as TiO₂ or a combination thereof can be added to the absorbent formulation to produce an absorbent with faster kinetics, as is illustrated in Fig. 31. The Example illustrated in Fig. 31 is a composite of CaO and TiO₂ (CaO:TiO₂=4:1) fabricated by spray drying and post-processing at 500°C for 3 hours.

From a practical point of view, the total absorption capacity in terms of CO₂ weight or weight percentage based on the total weight of the absorbent is more important. By comparing the effects of inert additives such as Al₂O₃ and MgO, both showing high initial capacity and stable recyclability at the proper composition and spray processing conditions, significantly improved results are achieved with respect to the total CO₂ capacity per gram absorbent by using only a small portion of 10 wt.% Al₂O₃ into CaO, as compared to CaO:MgO with 50 wt.% MgO. For example, Fig. 32 illustrates the absorption capacity for Examples A-22 and A-7 expressed as the total CO₂ capacity based on the mass of total absorbent. Each example has a relatively constant absorption capacity through 12 cycles and each is close to the theoretical value (66.78g CO₂/100g absorbent for A-22 and 39.28g CO₂/100g absorbent for A-7).

Fig. 33 illustrates the carbonation and decarbonation kinetics for four examples according to the present invention. It can be seen that the larger percentage of MgO in the CaO sample, the faster kinetics in the first carbonation region. Also the addition of Al₂O₃ can improve the kinetics in first carbonation region, as seen by comparing

Examples A-20 and A-22. The most rapid decarbonation kinetics occur with Example A-18.

Fig. 34 illustrates the particle size distribution before and after 12 cycles for certain CaO:MgO examples, with and without Al₂O₃ additions. Fig. 35 illustrates the pore volume, BET surface area and average pore diameter (pores < 100 nanometers) for the same examples. The presence of MgO effectively increases the porosity, particularly at high MgO contents, and maintains a small particle size.

Reforming Catalysts

To determine the feasibility of fabricating SMR catalysts by spray processing, powders having the composition 0.5 wt.% Rh supported on Al₂O₃ are produced using a spray processing method according to the present invention.

Example RC-1

This example illustrates the preparation of a 40g batch of 0.5% Rh/Al₂O₃ by spray pyrolysis. 4.2g of a 5 wt.% Rh(OAc)₃ solution is added while shearing to a solution formed from 200g of DISPAL 23N4-20 and 500g of de-ionized water. An additional 900g of de-ionized water is added to this mixture to dilute the solids loading to 2.5 wt.%. The total precursor dispersion is sheared for an additional 10 minutes. Spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 600°C, with air as the carrier gas and quench gas at 60 SLPM (standard liters per minute) and 5 SCFM (standard cubic feet per minute), respectively. This relates to a system having a reaction residence time of 1.5 seconds as calculated by the quotient of the system volume and the carrier gas flow rate corrected for temperature expansion.

Example RC-2

This example illustrates the preparation of a 40g batch of 0.5% Rh/Al₂O₃ by spray pyrolysis. 1.9g of a 10.6% Rh(NO₃)₃ solution is added while shearing to a solution formed from 200g of DISPAL 23N4-20 and 500g of de-ionized water. An additional 900g of de-ionized water is added to this mixture to dilute the solids loading to 2.5 wt.%. The total precursor dispersion is sheared for an additional 10 minutes. Spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of

600°C, with air as the carrier gas and the quench gas at 60 SLPM and 5 SCFM, respectively. This relates to a system having a reaction residence time of 1.5 seconds, as defined above.

5 **Example RC-3**

This example illustrates the preparation of a 300g batch of 0.5% Rh/Al₂O₃ by spray pyrolysis. 29.2g of a 5% Rh(OAc)₃ solution is added while shearing to a solution formed from 1492g of DISPAL 23N4-20 and 2kg of de-ionized water. An additional 2.4kg of de-ionized water is added to this mixture to dilute the solids loading to 5 wt.%.

10 The total precursor dispersion is sheared for an additional 10 minutes. Spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 600°C, with air as the carrier gas and as the quench gas at 60 SLPM and 5 SCFM, respectively. This relates to a system having a reaction residence time of 1.5 seconds, as defined above.

15

Example RC-3A

This example illustrates the preparation of a 40g batch of 0.5% Rh/Al₂O₃ by spray pyrolysis. 3.9 g of a 5% Rh(OAc)₃ solution is added to a solution of 200g of DISPAL 23N4-20 and 1.4kg de-ionized water while shearing. The resulting 5 wt.% solids precursor dispersion is sheared for an additional 10 minutes. The spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air carrier gas and quench at 60 SLPM and 5 SCFM, respectively. This relates to a system having a reaction residence time of 1.5 second as defined above.

20 Various other examples of reforming catalysts are prepared in a manner similar to the foregoing examples. All of these examples were prepared by spray pyrolysis. Table 9 lists the 0.5 wt% Rh/Al₂O₃ samples that are prepared by spray pyrolysis under different operating conditions. Each example is prepared from a precursor including Rh-nitrate or Rh-acetate and DISPAL 23 N4-20, except Example RC-7 which is prepared by post-treatment of Example RC-6.

30

Table 9

Sample	Composition	Solution (wt. %)	Temp. (°C)
RC-1	0.5% Rh/Al ₂ O ₃	2.5 Rh-acetate	600
RC-2	0.5% Rh/Al ₂ O ₃	2.5 Rh-nitrate	600
RC-3	0.5% Rh/Al ₂ O ₃	5 Rh-acetate	600
RC-4	0.5% Rh/Al ₂ O ₃	2.5 Rh-nitrate	500
RC-5	0.5% Rh/Al ₂ O ₃	2.5 Rh-nitrate	800
RC-6	0.5% Rh/Al ₂ O ₃	2.5 Rh-nitrate	500
RC-7	0.5% Rh/Al ₂ O ₃	N/A	600*
RC-8	0.5% Rh/Al ₂ O ₃	2.5 Rh-acetate	500
RC-9	0.5% Rh/Al ₂ O ₃	2.5 Rh-acetate	800
RC-10	0.5% Rh/Al ₂ O ₃	5 Rh-acetate	700
RC-11	0.5% Rh/Al ₂ O ₃	5 Rh-acetate	900
RC-12	0.5% Rh/Al ₂ O ₃	RC-3A	600*

* - Post-treatment at 600°C for 5 hours

5 The PSD, BET surface area, average pore diameter (pores < 100 nanometers) and pore volume are measured for Examples RC-1 and RC-2 and the results are listed in Table 10.

Table 10

Example	PSD d10, d50, d90 (μm)	BET Surface Area (m²/g)	Average Pore Diameter (nm)	Pore Volume (cm³/g)
RC-1	NA	221.3	5.9	0.324
RC-2	1.1, 1.7, 3.7	223.8	5.7	0.319

10 Catalytic activities are measured over Rh/Al₂O₃ catalysts prepared by spray processing under different operating conditions, which include different precursors, different precursor concentrations, and different processing temperatures as described in Table 9. The SMR activity of the powders is measured at a reaction temperature of

600°C and a H₂O:C ratio of 3:1. Compared to a standard commercially available reference catalyst with the same composition, the materials produced in this example show excellent performance, as can be seen in the following Figures.

Figs. 36 to 39 illustrate the effects of some spray processing parameters, including different precursors such as Rh-nitrate and Rh-acetate, different processing temperature and different concentration of the precursors, and post processing. These results are also compared to a commercial reference catalyst (Alfa Aesar, Ward Hill, MA) with identical amount of Rh supported on alumina.

Fig. 36 illustrates the conversion of methane in SMR over a 0.5 wt.% Rh/Al₂O₃ catalyst prepared by spray pyrolysis of Rh-nitrate and alumina gel at spray processing temperatures from 500°C to 800°C. The catalyst activity is clearly influenced by the spray processing temperature. Example RC-2 prepared at 600°C demonstrates better activity and has significantly better performance than the commercial catalyst. Post-processing of a catalyst at 500°C for 5 hours at 600°C significantly changes the SMR activity (compare Example RC-4 and RC-7) decreasing the conversion at lower space velocities and increasing the conversion at higher space velocities. This indicates that further changes in the activity/distribution of the active sites as well as in the pore structure of the catalyst can be introduced by post-processing.

The SMR results illustrated in Fig. 37 show a similar trend as seen in Fig. 36, although the precursor for spray processing is Rh-acetate. Again, 600°C is optimal for achieving the best performance and it is clear that spray processing has advantages for the preparation of a reforming catalyst as compared to conventional methods since all catalysts prepared by spray processing demonstrate higher conversion compared to the commercial catalyst.

Fig. 38 compares the SMR activity of 0.5 wt% Rh/Al₂O₃ prepared by spray pyrolysis when higher solids concentration was used in the spray processing suspension (5 wt.%) as compared to the samples from Fig. 37 (2.5 wt.%) and as function of the processing temperature (600°C, 700°C and 900°C). When the solids loading concentration is increased at the identical spray processing temperature (Example RC-3 compared to Example RC-1 in Fig. 37) the performance of the catalyst is lower. At higher solids loading, a higher spray processing temperature (900°C) forms

a catalyst with the best performance at high space velocities (Example RC-11). This result clearly demonstrates the flexibility of spray processing (variety of precursors, spray processing conditions and suspension solids loading) for the preparation of reforming catalysts with higher catalytic activity as compared to the catalyst prepared by a conventional approach.

Fig. 39 compares the CH_4 conversion for the best SMR catalysts made under different spray processing conditions with the commercial reference catalyst. It can be seen from Fig. 39 that all catalysts obtained from different conditions have superior catalytic activity than the commercial catalyst at all space velocities, and among them, the $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst made by spray processing at 600°C using Rh-acetate as a precursor and alumina gel at 2.5 wt.% solids loadings (Example RC-1) has the best performance over a wide range of space velocities.

These results also indicate that by using spray processing as a method for producing the SMR catalysts, it may be possible to reduce the precious metal content in these materials while maintaining or even improving overall performance. The results shown in Fig. 39 indicate that there is a strong connection between the spray-processing conditions and the structure and performance.

Multifunctional Catalysts

Two approaches can be used to make multifunctional particles containing an absorbent and an SMR catalyst. The final powders can be generated by either spray drying or spray pyrolysis, starting with either combinations of powders or combinations of precursors and powders.

One method combines individual $\text{CaO}:\text{MgO}$ and $\text{Rh}/\text{Al}_2\text{O}_3$ powders, preferably powders that are made by either spray drying or spray pyrolysis. The individual powders are dispersed together in a carrier such as water and processed through a spray dryer or a spray pyrolysis unit. For example, in the first row of Table 11 below, both powders are made on a spray dryer, and the powders are then dispersed in water and spray dried again. In another example, the catalyst represented in the second row is made by combining $\text{CaO}:\text{MgO}$ powder from spray pyrolysis with $\text{Rh}/\text{Al}_2\text{O}_3$ powder from a spray dryer in water, then processing the combined powders on a spray dryer.

Table 11

CaO:MgO Powder	Rh/Al₂O₃ Powder	Processing
Spray Dryer	Spray Dryer	Spray Dryer
Spray Pyrolysis	Spray Dryer	Spray Dryer
Spray Dryer	Spray Dryer	Spray Pyrolysis
Spray Pyrolysis	Spray Dryer	Spray Pyrolysis
Spray Dryer	Spray Pyrolysis	Spray Dryer
Spray Pyrolysis	Spray Pyrolysis	Spray Dryer
Spray Dryer	Spray Pyrolysis	Spray Pyrolysis
Spray Pyrolysis	Spray Pyrolysis	Spray Pyrolysis

The second approach, summarized in Table 12 below, combines powders and precursors with different processing systems. Component powders are generated by either spray drying or spray pyrolysis. The powder is then combined with the precursors to the remaining component and processed.

In Table 12, the word 'Precursors' indicates that the final catalyst is made by adding precursors to a powder, followed by a final processing. In the first row of Table 12, Rh/Al₂O₃ is separately made on a spray dryer and combined with the precursors to CaO:MgO. The resulting mixture is then processed on a spray dryer to yield a multifunctional catalyst. In the fifth row, the CaO:MgO is made on a spray dryer and combined with the precursors to Rh/Al₂O₃. The resulting mixture is then processed on a spray dryer to yield a multifunctional catalyst.

Table 12

CaO:MgO	Rh/Al₂O₃	Processing
Precursors	Spray Dryer	Spray Dryer
Precursors	Spray Pyrolysis	Spray Dryer
Precursors	Spray Dryer	Spray Pyrolysis
Precursors	Spray Pyrolysis	Spray Pyrolysis
Spray Dryer	Precursors	Spray Dryer
Spray Pyrolysis	Precursors	Spray Pyrolysis
Spray Dryer	Precursors	Spray Pyrolysis
Spray Pyrolysis	Precursors	Spray Dryer
Precursors	Precursors	Spray Dryer
Precursors	Precursors	Spray Pyrolysis

The following illustrate certain examples of the fabrication of multi-functional composite materials in more detail.

Example MC-1

5 This example illustrates the fabrication of a 1kg batch of CaO:MgO (55:45 ratio) and 0.5% Rh/Al₂O₃ having a net composition of 90%CaO:MgO and 10% SMR catalyst according to the present invention. 0.96kg of CaC₂O₄:MgC₂O₄ (55:45 ratio and fabricated on a spray dryer) is dispersed in 4 kg of de-ionized water. 39.8g of 0.5% Rh/Al₂O₃ fabricated on a spray dryer and an additional 4kg of de-ionized water is added,
10 and the mixture is shear mixed for 30 minutes. The precursor dispersion is fed into a mixed flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system used is 10 seconds as defined above. The powder is collected using a cyclone.

Example MC-2

15 This example illustrates the fabrication of a 1kg batch of CaO:MgO (55:45 ratio), 0.5% Rh/Al₂O₃ having a net composition of 90%CaO:MgO and 10%SMR catalyst according to the present invention. Individually, 0.83kg of calcium nitrate is dissolved in
20 1kg of de-ionized water, 0.81 kg of ammonium oxalate in 2kg of de-ionized water, 1.0kg of magnesium nitrate in 1 kg of de-ionized water, and 0.92kg of ammonium oxalate in 2kg of de-ionized water. These solutions are shear mixed for 30 minutes. The calcium nitrate solution is added to the smaller ammonium oxalate solution and the magnesium nitrate solution is added to the larger. The precipitates are shear mixed individually for
25 an hour, then combined. 39.8g of 5 wt.% Rh/Al₂O₃ (made in a spray dryer) is added to the precipitate mixture, and the resulting 10 wt.% solids precursor is shear mixed for one hour. The precursor dispersion is fed into a mixed flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system is 10 seconds, as defined
30 above. The powder is collected using a cyclone.

Example MC-3

This example illustrates the fabrication of a 1kg batch of CaO:MgO (55:45 ratio) and 0.5% Rh/Al₂O₃ having a net composition of 90% CaO:MgO and 10% SMR catalyst according to the present invention. Individually, 0.83kg of calcium nitrate is dissolved in 1kg of de-ionized water, 0.81 kg of ammonium oxalate in 2kg of de-ionized water, 1.0kg of magnesium nitrate in 1 kg of de-ionized water, and 0.92kg of ammonium oxalate in 2kg of de-ionized water. These solutions are shear mixed for 30 minutes. The calcium nitrate solution is added to the smaller ammonium oxalate solution and the magnesium nitrate solution is added to the larger. The precipitates are shear mixed individually for an hour, then combined and sheared for 30 minutes. 3.9g of a 5 wt.% Rh(OAc)₃ solution is sheared into 198g of DISPAL 23N4-20, then slowly added to the calcium and magnesium oxalates mixture. This resulting 10 wt.% solids precursor is shear mixed for an additional 30 minutes. The precursor dispersion is fed into a mixed flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system used is 10 seconds as defined above. The powder is collected using a cyclone.

Example MC-4

This example illustrates the fabrication of a 30g batch of CaO:MgO (55:45 ratio) and 0.5% Rh/Al₂O₃ having a net composition of 90% CaO:MgO and 10% SMR catalyst according to the present invention. Individually, 56.7g of calcium nitrate is dissolved in 200g of de-ionized water and 85.8g of magnesium nitrate in 200g of de-ionized water. 0.3g of a 5 wt.% Rh(OAc)₃ solution is sheared into 15g of DISPAL 23N4-20 and 500g of de-ionized water. The calcium and magnesium solutions and 140g of de-ionized water are sheared into the Rh/Al₂O₃ dispersion. This resulting 2.5 wt.% solids precursor is shear mixed for an additional 10 minutes. Spray pyrolysis is conducted using an ultrasonic transducer system at a furnace temperature of 900°C, with air carrier gas and quench at 70 SLPM and 6 SCFM, respectively. The system has a reaction residence time of 0.9 second, as defined above.

Example MC-5

This example illustrates the fabrication of a 1kg batch of CaO:MgO (80:20 ratio) and 0.5% Rh/Al₂O₃ having a net composition 90% CaO:MgO and 10% SMR catalyst according to the present invention. 0.96kg of CaC₂O₄:MgC₂O₄ (80:20 ratio and made on a spray dryer) is dispersed in 4 kg of de-ionized water. 41.8g of 0.5% Rh/Al₂O₃ (made by spray pyrolysis) and an additional 5kg of de-ionized water is added, and the mixture is shear mixed for 30 minutes. The precursor dispersion is fed into a mixed flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system used is 10 seconds, as defined above. The powder is collected using a cyclone.

Example MC-6

This example illustrates the fabrication of a 1kg batch of CaO:MgO (55:45 ratio) and 0.5% Rh/Al₂O₃ having a net composition of 90% CaO:MgO and 10% SMR catalyst according to the present invention. Individually, 0.83kg of calcium nitrate is dissolved in 1.5kg of de-ionized water, 0.81 kg of ammonium oxalate is dissolved in 2kg of de-ionized water, 1.0kg of magnesium nitrate is dissolved in 0.5kg of de-ionized water, and 0.92kg of ammonium oxalate is dissolved in 2kg of de-ionized water. These solutions are shear mixed for 30 minutes. The calcium nitrate solution is added to the smaller ammonium oxalate solution and the magnesium nitrate solution is added to the larger. The precipitates are shear mixed individually for an hour, then combined and sheared for 30 minutes. 39.8g of 0.5% Rh/Al₂O₃ (made via spray pyrolysis) is slowly added to the calcium and magnesium oxalates mixture. The resulting 10 wt.% solids precursor is shear mixed for an additional 30 minutes. The precursor dispersion is fed into a mixed flow spray dryer at a liquid feed rate to maintain inlet/outlet temperatures of 975°F/580°F, using a two-fluid nozzle with an air pressure of 65 psig. The residence time of the system used is 10 seconds, as defined above. The powder is collected using a cyclone.

Table 13 provides some physical characterization data for the materials described in the examples above.

Table 13

Sample	PSD d10, d50, d90 (μm)	BET Surface Area (m^2/g)	Pore Diameter (nm)	Pore Volum (cm^3/g)
MC-2	1.8, 4.1, 8.8	31.3	11.1	0.087
MC-3	1.6, 3.8, 8.4	18.8	11.7	0.055
MC-4	1.6, 3.8, 8.1	7.5	13.1	0.025
MC-5	1.8, 5.3, 12.9	56.8	10.8	0.154
MC-6	1.7, 3.9, 8.0	33.2	10.3	0.086

5 Additional examples of multi-functional absorbent/catalysts are prepared, as listed in Table 14. Each of the multi-functional absorbent/catalysts was a composite powder batch including 90 wt.% CaO:MgO (50:50 by wt.) and 10 wt.% of a 0.5 wt.% Rh/Al₂O₃ SMR catalyst. Each of the Examples was prepared by spray pyrolysis using

10 ultrasonic transducers.

Table 14

Example	Process Conditions	Precursor Composition
MC-7	Spray Pyrolysis (500°C)	Ca-nitrate Mg-nitrate Rh-acetate DISPAL 23N4-20
MC-8	Spray Pyrolysis (500°C) Post-process (500°C)	MC-7
MC-9	Spray Pyrolysis (700°C)	Ca-nitrate Mg-nitrate Rh-acetate DISPAL 23N4-20
MC-10	Spray Pyrolysis (900°C)	Ca-nitrate Mg-nitrate Rh-acetate DISPAL 23N4-20
MC-11	Spray Pyrolysis (900°C)	Ca-nitrate Mg-nitrate Rh-acetate DISPAL 23N4-20

The precursor solution for Example MC-11 is allowed to sit overnight to enable the Rh-acetate precursor to absorb onto the alumina surface.

15 The multi-functional materials are first tested for their absorption characteristics. Fig. 40 illustrates the absorption capacity over 24 cycles for Examples MC-8, MC-9,

MC-10 and MC-11. Example MC-11 had the highest CO₂ absorption capacity and had very little loss in capacity over multiple cycles.

Fig. 41 illustrates the comparison of the carbonation/decarbonation kinetics profile for Examples MC-8, MC-9, MC-10 and MC-11. A comparison of the decarbonation rates for the multifunctional materials containing absorbent and catalysts made by spray pyrolysis simultaneously (Fig. 41) with those of materials without catalyst (Fig. 30) shows that the former have substantially faster decarbonation rates. Therefore, the production of combined functionality materials by spray methods offers higher level of flexibility in the control over the decarbonation rates.

Figs. 42 and 43 illustrate the cyclability of Example MC-10 over 92 cycles. These Figures illustrate that the multi-functional materials have a high CO₂ absorption capacity and maintain a level absorption performance over at least 92 cycles. Fig. 44 illustrates the kinetics of carbonation and decarbonation for Example MC-10 over 80 cycles. The kinetics show a rapid desorption kinetics of the CO₂ which stays substantially unchanged over 80 cycles.

Pelletization

The following illustrates CO₂ absorbent performance after pelletizing and how the selected powder precursors for pellet extrusion affect CO₂ absorption by altering the microstructure and porosity.

Table 15 summarizes examples of extruded pellets made from powders that were produced on a spray dryer without further post-processing (see Tables 4 and 5 for the synthesis conditions). Among the extrudates, the binder (boehmite alumina) used for extrusion is kept the same.

Table 15

Example	Powder Composition	Extrudate
A-2	Ca-oxalate	C28-41-18
A-3	Ca-oxalate 5% Al ₂ O ₃	C28-41-20
A-3A	Ca-oxalate 25% Al ₂ O ₃	C28-41-22
A-6	CaO:MgO (50:50 wt.%)	C28-41-24
A-7	CaO:MgO (50:50 wt.%) 5% Al ₂ O ₃	C28-41-26
A-19	CaO:MgO (90:10 wt.%)	C28-41-28
A-21	CaO:MgO (90:10 wt.%) 5% Al ₂ O ₃	C28-41-32

Figs. 45 and 46 illustrate the carbonation performance of extrudates formed from precursors including calcium oxalate or calcium carbonate. Fig. 45 illustrates the CaO reaction fraction and Fig. 46 shows the total CO₂ capacity in mass CO₂ per mass of absorbent. After pelletization, CaO reactivity to CO₂ carbonation decreases due to microstructural changes caused by the presence of a binder. In the case of sample C28-41-22 the activity to CO₂ carbonation is very low due to the use of large amount of Al₂O₃ in the powder precursor sample, similar to the results described for the non-pelletized powder. The presence of a large amount of Al₂O₃ will possibly cause it to react with CaO to form a new phase such as a spinel structure and prevent access of CO₂ to unreacted CaO.

Fig. 47 illustrates a comparison of the carbonation and decarbonation kinetics for selected extrudates.

Fig. 48 illustrates the absorption capacity over 116 cycles of Extrudate C28-41-32, which is pelletized from a powder made by spray drying with a composition of Ca-oxalate and Mg-oxalate precursor containing 5 wt.% Al₂O₃. It can be seen that CaO reactivity to CO₂ carbonation is around 40 mol.% and is very stable over the 116 cycles of the test. (The dips in absorption at cycle numbers 60 and 108 are due to the depletion of the CO₂ source during testing). The absolute capacity for CO₂ absorption illustrated in Fig. 49 during the same cycling test is around 23 to 25 grams CO₂/per 100 grams of extrudate.

Table 16 lists the powders made from spray pyrolysis used for additional pelletization testing.

Table 16

Sample	Composition	Extrudate
A-14	CaO	C2873-3-29
A-15	CaO	C2873-3-25
A-23	CaO:MgO (50:50 at.%)	C2873-3-31
A-24	CaO:MgO (50:50 at.%)	C2873-3-33
A-25	CaO:MgO (50:50 at.%)	C2873-3-35
A-26	CaO:MgO (50:50 at.%)	C2873-3-27

5 The details of the powder preparation conditions are listed in Tables 4 and 5. The amount of the binders used for extrusion for these powders are all kept the same. Figs. 50 and 51 show the results of CO₂ carbonation reactivity and cyclability over the extrudates. Fig. 50 illustrates the CaO reaction fraction over multiple cycles. For the Examples illustrated in Figs. 50 to 62, carbonation occurs at 600°C and decarbonation
10 occurs at 800°C. At the initial stage, the CaO reactivity is higher, then gradually becomes stable and levels at around 60 mol.% during multiple cycles. As compared to the extrudates from CaO:MgO, the extrudates from CaO (C2873-3-29 and C2873-3-25) have a low stability and the absorption capacity gradually decreases during multiple cycles.

15 Fig. 51 illustrates the total CO₂ capacity over the same cycle test as illustrated in Fig. 50. The capacity for the extrudates made from CaO powders (C2873-3-29 and C2873-3-25) is higher than the extrudates made from CaO:MgO powders (C2873-3-31, C2873-3-33, C2873-3-35 and C2873-3-27). However, the extrudates from CaO:MgO powders show more stable recyclability and the capacity for CO₂ removal is around 22 g
20 CO₂ per 100 g absorbent.

 Figs. 52 and 53 illustrate the cyclability of Extrudate 2872-3-27 over 100 cycles. Fig. 52 illustrates the CaO reaction fraction and Fig. 53 illustrates the total CO₂ capacity. (The deviations at Cycles 40 and 72 are due to depletion of the CO₂ source during testing). This extrudate maintains a high absorption capacity over at least 100 cycles.

25 Pellets can also be formed from powders made by spray drying and post-processing according to the present invention. Table 17 lists several such examples.

Table 17

Extrudate	Powder Composition	Process Conditions
C2873-29-32	CaO:MgO (50:50 by wt.)	SD, PP at 500°C
C2873-29-34	CaO:MgO (50:50 by wt.)	SD, PP at 750°C
C2873-30-25	CaO:MgO (50:50 by wt.)	SD, PP at 500°C
C2873-31-33	95% CaO 5% CaTiO ₃	SD, PP at 750°C
C2873-32-30	CaO:MgO (50:50)/CaTiO ₃ (3/1 by at.)	SD, PP at 650°C
C2873-33-33	CaO/CaTiO ₃ (3/1 by at.)	SD, PP at 750°C
C2873-34-30	Ca-oxalate 5 wt.% Al ₂ O ₃	SD, PP at 500°C
C2873-35-31	Ca-oxalate 5 wt.% Al ₂ O ₃	SD, PP at 750°C
C2873-50-24	CaO:MgO (80:20 by wt.)	SD, PP at 500°C
C2873-50-26	CaO:MgO (80:20 by wt.)	SD, PP at 500°C

Figs. 54 and 55 illustrate the reactivity and cyclability of extrudate C2873-29-32 made from the powder with CaO/MgO (50:50 wt. ratio) followed by post processing at 500°C. Fig. 54 illustrates the CaO reaction fraction over 66 cycles and Fig. 55 illustrates the CO₂ capacity for the same cycle tests. The dips in CaO reaction fraction (e.g., at Cycle 42) is believed to be due to a depletion of the CO₂ source. These figures demonstrate that the absorbent powder formed by spray drying and post-processing at 500°C can be formed into a pellet having a high absorption capacity over a large number of cycles.

Figs. 56 and 57 illustrate the reactivity and cyclability of extrudate C2873-29-34 made from the powder with CaO:MgO (50:50 wt. ratio) followed by post processing at 750°C. Fig. 56 illustrates the CaO reaction fraction over 66 cycles and Fig. 57 illustrates the CO₂ capacity for the same cycle tests. These examples were tested at the same time as the examples illustrated in Figs. 54 and 55, and the dips in CaO reaction fraction (e.g., at Cycle 42) is believed to be due to a depletion of the CO₂ source. These figures demonstrate that the absorbent powder formed by spray drying and post-processing at 750°C can be formed into a pellet having a high absorption capacity over a large number of cycles.

Figs. 58 and 59 illustrate the reactivity and cyclability of extrudate C2873-32-30 made from the powder with CaO:MgO (50:50 wt. ratio) containing 33 mol% of CaTiO₃ followed by post processing at 750°C. Fig. 58 illustrates the CaO reaction fraction over 66 cycles and Fig. 59 illustrates the CO₂ capacity for the same cycle tests. Again, the dips in capacity (e.g., at cycles 17, 30 and 38) are due to depletion of the CO₂ source.

Figs. 60 and 61 illustrate the cyclability of extrudate C2873-35-31 made from the powder with 10 wt.% Al₂O₃ followed by post processing at 750°C. Fig. 60 illustrates the CaO reaction fraction over 64 cycles and Fig. 61 illustrates the CO₂ capacity for the same cycle tests.

Fig. 62 illustrates the CaO reaction fraction for Extrudate C2873-34-30 made from the powder with 10 wt.% Al₂O₃ followed by post processing at 500°C over 64 cycles.

Performance of Multi-Functional Composites

Fig. 63 illustrates the cycling results of steam methane reforming over materials according to the present invention, namely a combination of mechanical mixing of SMR catalysts (C2873-19-31, which is extruded from a powder containing 0.5 wt.% Rh) with CaO-based reversible CO₂ absorbents, namely the combination of pellets, which are extruded from powders of calcium oxalate containing 5% Al₂O₃ and CaO. The weight ratio of catalyst to absorbent is 1:5. The steam reforming of methane is conducted under conditions of H₂O:C of 3:1 and a temperature of 600°C.

Fig. 64 illustrates that with a single step, hydrogen-containing gas can be produced with a H₂ purity of more than 96% (dry basis). The CO is around 1.0 mol.% and CO₂ is less than 0.5 mol.%. The high and stable hydrogen concentration as a function of cycle number demonstrates the utility of the materials according to the present invention. These results are significantly different from the conventional steam methane reforming, in which the reformat typically includes only about 45% to 55% hydrogen (dry basis), and more than 20% carbon oxides including about 10% CO.

While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur

to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention.